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A DIVISION OF
AEROJET-GENERAL CORPORATION

THE DEVELOPMENT OF NEW AND/OR IMPROVED AQUEOUS PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

FINAL REPORT
VOLUME II

PREPARED UNDER CONTRACT PH 86-68-77

SUBMITTED TO

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CINCINNATI, OHIO

AEROJET-GENERAL CORPORATION
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Efficient absorption of SO2 at flue gas concentrations can be effected through the use of dry, fluidized basic materials in the range of 50 to 60 C, if sufficient water is incorporated into the gas phase upstream of sorbent contactor. The formation of sulfate can be essentially eliminated in a fluidized bed absorber, and reduced to a very low value in an aqueous absorber, through the use of ferrous ion in an aqueous prescrubber to reduce NO2 to NO. The thermal decomposition of both zinc and magnesium sulfites is markedly promoted by the presence of steam. A new process for the removal of SO2 from flue gas is described in which dry fluidized zinc oxide is used as the absorbent. The oxide is recovered for reuse upon thermal decomposition of the resulting sulfite, and the liberated SO2 is recovered as such. Little or no sulfate is formed. NOx (especially NO2) is the major contributor to oxidation of the sorbent in aqueous solution systems. In general, the inhibitors and complexing agents investigated did not lower the level of oxidation in the presence of NOx in the flue gas. The level of oxidation is less in sorbent solutions saturated with an inert salt. The efficiency of SO2 removal from flue gas is not affected by the presence of NOx. The economics of the conceptualized fluidized-bed zinc oxide process appear to be superior to other regenerable processes for the removal of SO2 from flue gases, but the state of development of this process is in its very early stage.

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FINAL REPORT

VOLUME II

October 1970

by

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Prepared under Contract PH 86-68-77 by the
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PART ONE

GENERAL

I. INTRODUCTION

The initial objective of Contract No. PH 86-68-77 was to assay the feasibility of using aqueous systems for removing sulfur dioxide from flue gases. The period of service of the initial program was from 29 December 1967 to 31 May 1969. This technical effort is reported in Volume I, "Applicability of Aqueous Solutions to the Removal of SO_2 from Flue Gases." An extension of this program covered the period 31 May 1969 to 1 September 1970. This part of the program is reported in Volume II, "The Development of New and/or Improved Aqueous Processes for Removing SO_2 from Flue Gases."

The general discussion, Part One, consisting of the Introduction, and Summary and Conclusions, is identical in both volumes of this report and provides a resume of the entire project.

The following three phases define the program effort of the initial period:

Phase I. Assessment of Aqueous Solution Methods

- Literature survey
- Preliminary economic evaluation for comparative purposes
- Selection of Candidate processes

Phase II. Laboratory Experimentation Relating to Candidate Processes

- Process simplification and improvement of each candidate existing process
- Demonstration of process feasibility of any candidate new process

Phase III. Preliminary Plant-Scale Process Evaluation and Cost Estimates for the Candidate Processes

- Application of processes selected on the basis of Phases I and II to both new and existing power plant facilities
- Application of processes selected on the basis of Phases I and II to a new smelter facility.

Phase I was accomplished during the first five months of 1968 with Phases II and III conducted concurrently during the remainder of the calendar year.

The following parts of Volume I are concerned with the results of the application of the various tasks listed above. Parts Two to Four cover the work conducted under Phases I, II, and III, respectively. Part Five discusses recommendations for future work under the contract extension. Part Six, "Bibliography" is the result of the extensive literature survey which was carried out at the beginning of Phase I. Nearly 700 references are listed, together with an appropriate author index.

The program extension, designated as Phase IV, consisted of the following tasks:

A. Conceive New Aqueous Scrubbing Processes,

B. Develop Improvements to Previously Conceived Aqueous Scrubbing Processes,

C. Determine the Degree to Which Inadvertent Sorbent Oxidation Can Be Minimized;

D. Determine the Degree of Interference Which Inadvertent Sorption of NO_x Has On SO_2 Removal Efficiencies; and

E. Support the Laboratory Investigations with Preliminary Process Evaluations and Economic Analyses.

The tasks of Phase IV are covered in Parts Two through Six of Volume II.

II. SUMMARY AND CONCLUSIONS

A. VOLUME I

Approximately 500 technical documents, selected from the bibliography of Part Six, were collected, catalogued, and reviewed for the identification and description of various aqueous processes which have been used, or are currently being investigated, developed, or used for the removal of sulfur dioxide from flue gases. Some thirty processes were identified, and of these sufficient data were available for a preliminary economic evaluation of twenty-two. As a result of the evaluation the following four processes were considered to merit further investigation:

- Zinc Oxide Process (Sodium Sulfite Scrubbing)
- Cominco Exorption Process (Ammonium Sulfite Scrubbing)
- Ammonia-Hydrazine Exorption Process (Hydrazine Scrubbing)
- Mitsubishi Lime Process (Lime water Scrubbing)

The Ammonia-Hydrazine Exorption process, conceived at Aerojet, represented a paper study, subject to an experimental demonstration of process feasibility.

Following process selection, a laboratory program was conducted relating to process demonstration and/or improvement. Attempts to improve the Zinc Oxide process were mainly concerned with lowering the calcination temperature required for the release of sulfur dioxide from the regeneration feed, zinc sulfite. No significant improvements were effected, but the investigation led to the conception of a new process based on the use of zinc oxide, in which a fluidized bed of this material is used directly for the low-temperature (50°C) sorption of sulfur dioxide. The feasibility of the concept was demonstrated in the laboratory.

The Cominco Exorption process suffers from the relatively high steam costs associated with the desorption of sulfur dioxide from aqueous ammonium bisulfite solution. The use of acids as promoters for this reaction was therefore investigated. Although several acids were found to be partially effective it was found that the cost of the acid, the additional complexity to the process caused by the use of the acid, and other factors would not be compensated by the limited reduction in steam requirements which might be attainable in this manner. It was concluded, therefore, that this process must be considered as uneconomical.

The Ammonia-Hydrazine Exorption process was designed to combat the high steam requirements of the Cominco Exorption process through the use of hydrazine as the absorbent for sulfur dioxide. Since hydrazine salts are highly soluble in aqueous media it appeared that the desorption of sulfur dioxide from aqueous hydrazine bisulfite might be effected without the simultaneous volatilization of large quantities of water. As the result of an experimental program designed to demonstrate process feasibility, it was found that concentrated hydrazine sulfite solution readily absorbed sulfur dioxide under simulated process conditions. However, an unavoidable loss of hydrazine by oxidation occurred during the regeneration reaction, so that any savings in steam costs through the use of this method was nullified. Therefore, the process was no longer regarded as economically feasible.

No experimental work was indicated relating to the Mitsubishi Lime process. The process was regarded as economical, provided that by-product gypsum could be sold in quantity. However, a subsequent market survey indicated that gypsum requirements could readily be filled from natural deposits and that no appreciable synthetic gypsum market exists at the present time. A simplified version of the process, in which the gypsum is discarded as waste, appeared more attractive. A laboratory effort was not considered to be needed for the simplified process.

In addition to the laboratory effort described above, which was designed to overcome problems associated with specific processes, some attention was also directed to a problem which is common to all aqueous scrubbing methods in which sulfur dioxide is recovered as such; namely, the oxidation of sulfite to sulfate in the absorber. The literature indicates that in some processes oxidation can amount to 10 to 14% or more (expressed as a percentage of the incoming SO_2). It was planned to investigate the extent to which oxygen and nitrogen oxides in flue gas contribute to oxidation, and to investigate the use of various oxidation inhibitors, such as hydroquinine, for its prevention. Work in this area was initiated toward the end of the contract period, and was completed during the second year of the program (Phase IV). The results are reported in Volume II.

Of the four candidate processes, only the Zinc Oxide process (Na^+ scrubbing/ZnO regenerant) was considered for a complete evaluation in Phase III. Thus, process evaluations and cost estimates were completed for large new and existing power plants, a small existing power plant, and for an existing smelter facility. An evaluation was begun on the simplified lime process, but was not completed since the analysis of limestone systems was being done on another contract.

The major conclusions which were drawn from the work reported in Parts Two to Four of Volume I, are the following:

- Of the four candidate processes which were selected for further study as the result of the Phase I effort, the Zinc Oxide process was considered to merit further study, both in the form of a fluidized bed system, as proposed by Aerojet, and in the form of the original Na^+ scrubbing process, as developed by Johnstone to the small-scale pilot stage. For the Johnstone process available data in Phase III indicated that for a large power plant (2.5 MMSCFM of flue gas) to be operated at break-even conditions, product sulfuric acid would have to be salable at almost \$25/ton (assuming a 70% load factor and an SO_2

feed gas concentration of 3000 ppm). If, however, the product acid from this plant could be sold for only \$10/ton, the operation of this "add-on" SO_2 control process would represent a net cost to the utility of about \$1.23/ton of coal burned. Applied to a medium-sized smelter effluent (220,000 SCFM of the flue gas), the Johnstone process could be operated at break-even conditions, if product sulfuric acid were sold at about \$18/ton.

- The three remaining candidate processes (Cominco Exorption, Ammonia-Hydrazine Exorption, and Mitsubishi Lime) are not considered to be as economically attractive as the Johnstone process.
- A major problem confronting any aqueous process in which sulfur dioxide is recovered as such is that of oxidation in the scrubber. Such oxidation inevitably leads to the formation of sulfate, which is in general less readily isolated from aqueous solution and less readily decomposed than the corresponding sulfite. As a result it may be anticipated that equipment and operating costs will increase, and product yields will decrease, in proportion to the extent of oxidation encountered.

B. VOLUME II

In the area relating to new aqueous processes for the removal of SO_2 from flue gas, attention has been focused on the use of fluidized solids as absorbents. The absorption step, which is conducted at 50° to $60^\circ C$, requires the presence of appreciable water in the gas phase, and this is provided largely through the use of an aqueous prescrubber. The prescrubber also serves the function of removing SO_3 and fly ash from the raw gas.

Only basic materials have proved suitable as SO_2 absorbents. It was found, for example, that both alkali (Na, K) and alkaline earth (Mg, Ca) sulfites are too weakly basic to absorb, but that carbonates (Na) and oxides (Zn, Mg) are good absorbers. For example, when zinc oxide was used it was found that more than 50 g of SO_2 was absorbed per 100 g of the oxide before SO_2 removal efficiency dropped below 90%.

A problem that arises in all regenerative aqueous SO_2 scrubbing processes is that a portion of the absorbent becomes oxidized by the O_2, fly ash, and/or NO_x components of flue gas. This is highly undesirable, inasmuch as the absorbent cannot readily be regenerated for reuse from the oxidized product. The extent of oxidation appears to be substantially less for essentially dry fluidized bed absorbents than for bulk water systems, and in particular fly ash, which tends to catalyze the oxidation in bulk water systems, was determined to be without effect when incorporated into a dry fluidized zinc oxide absorber.

Of the three gaseous oxidizing components of flue gas (O_2, NO, and NO_2), it was found that NO_2 is by far the most active, and that fluidized zinc oxide was partially converted to sulfate when both SO_2 and NO_2 were present in the influent gas. It was discovered, however, that oxidation of the bed material could be essentially eliminated through the incorporation of ferrous ion into the aqueous prescrubber. The main function of the ferrous ion is considered to be that of reducing NO_2 to NO. For an influent gas containing all flue gas components, less than one-half percent of the SO_2 absorbed by zinc oxide was converted to sulfate when the prescrubber contained 1% ferrous sulfate. In the practical case, ferrous ion would be provided to the prescrubber in the form of scrap iron.

It may be presumed that the use of fluidized solids as SO_2 absorbents will be attended to some extent by the attrition of solid particles, and consequently some attention was devoted to a study of both particle size and particle activity when zinc oxide was used as the absorbent. It was found that commercially available, large pelleted oxide particles are readily attrited to fine particles, but that if the oxide is first converted to the sulfite through SO_2 absorption, and the sulfite is then thermally decomposed, the resulting regenerated oxide shows considerable resistance to attrition. Recent studies have indicated that both zinc sulfite and regenerated zinc oxide in the range of -12 to +24 mesh can be utilized with considerable resistance to attrition at a superficial gas velocity of about 3 feet per second. It was also found that the regenerated oxide is much more active toward SO_2 absorption than is the fresh, unused commercially available oxide.

In the area relating to process improvement, attention was directed toward the thermal decomposition of metallic sulfites, inasmuch as these compounds are the principal products resulting from the absorption of SO_2 by metallic oxides and hydroxides, and because the regeneration of the oxides from the sulfites is probably best accomplished by thermal means. The decomposition reaction is always attended to some extent by the formation of sulfate, and other products, as a result of the disproportionation of the sulfite.

The thermal decomposition of zinc sulfite was studied in both muffle and tube furnaces as a function of time and temperature. An important result of this work was the discovery that the rate of the decomposition reaction was markedly increased in the presence of steam. It was subsequently found that the use of steam permitted the decomposition to be carried out at temperatures ($<300^\circ C$) below which disproportionation occurs, so that the formation of sulfate and sulfide could be essentially avoided. In another series of experiments it was found that the use of steam was much less effective in promoting the decomposition of zinc sulfate.

The disproportionation of magnesium sulfite is more extensive than that of zinc sulfite, and it might be expected that the use of steam would be less effective in the case of magnesium. Preliminary experiments have shown that the temperatures required for the decomposition of magnesium sulfite are substantially decreased through the use of steam, but that the formation of appreciable sulfate attends the decomposition.

As a result of the experimental work considered above relating to the use of fluidized zinc oxide as an absorbent for SO_2, a tentative system was formulated involving the recovery of the SO_2 as such. The overall system involves the use of an aqueous prescrubber, the removal of SO_2 from the water-saturated gas by the oxide, and the thermal decomposition of the resulting sulfite at 275°C for the regeneration of the oxide and the recovery of SO_2. Any zinc sulfate formed is separately decomposed at higher temperatures, and no waste product results. In an alternative system, sulfate is removed by filtration rather than by calcination. To accomplish this, a portion of the sulfite-sulfate mixture is dissolved in aqueous SO_2 and the sulfite is reprecipitated with zinc oxide. After filtering the zinc sulfate solution, the sulfite cake is returned to the process.

The studies on oxidation and oxides of nitrogen in aqueous solution scrubbing systems were combined due to the contributions of nitrogen oxides to sorbent oxidation. Most of the experiments were made with sodium sulfite-bisulfite solutions similar to that used in the Johnstone Zinc Oxide process. A "once through" countercurrent absorption column was used in most of these tests. Fresh absorbent solution was fed to the top of the column and the spent solution removed from the bottom. Another arrangement was used for some tests in which the absorbent was recirculated through the column. Other absorbent systems checked were potassium sulfite-bisulfite, and magnesium, calcium, and sodium hydroxide solutions.

Commercially available inhibiting and complexing agents, widely used in other applications, were screened for their ability to reduce oxidation of sulfur dioxide (sorbent) in the scrubber. Oxidation of the sorbent due to oxygen or fly ash in the flue gas was suppressed by some of the materials. When nitrogen oxides were present in the flue gas, however, oxidation was lowered only by using nitrilotriacetic acid, and this inhibitor was effective only in a potassium sulfite-bisulfite solution having a pH of 12.6.

It was found that, although oxygen in the flue gas contributes to the oxidation of the sorbent during scrubbing, the high levels of oxidation was progressively greater as the concentration of nitrogen dioxide in the flue gas was increased. The rate of oxidation was highest in tests made with 400 ppm each of nitrogen oxide and nitrogen dioxide.

Fly ash did not significantly increase oxidation in systems where fly ash free absorbents were fed to the once through column. In absorbent recirculating systems, in which the fly ash accumulated and some of the iron content was solubilized, a low level of SO_2 oxidation was experienced. The oxidation increased with increasing turbulence in the system. A similar effect was found when ferric ions such as $Fe_2(SO_4)_3$ were added to the system.

Saturating the sodium sulfite-bisulfite scrubbing solution with sodium sulfate inhibits oxidation. This is explained by the limited solubility of oxygen in high ionic strength aqueous solutions.

Since oxygen is only slightly soluble in water, the liquid phase is the limiting resistance to the absorption of the oxygen. Thus, increasing turbulence in the scrubber improves the absorption of oxygen and the amount of oxidation of the sorbent increases with the turbulence of the system.

As discussed in Part Three, a prescrubber circulating a solution containing ferrous ion removes the nitrogen dioxide from the flue gas stream. Using this prescrubber system in conjunction with aqueous solution scrubbers also reduced oxidation of the sorbent to a very low level due to removal of the nitrogen dioxide.

Although additional investigations would be needed to verify the data, it seems that the absorption of nitrogen oxides simultaneously with sulfur dioxide is about the same quantity as the percent nitrogen dioxide in the flue gas. The experiments also indicate that the absorption of NO_x into SO_2 scrubbing solutions has no effect on SO_2 removal efficiency.

Miscellaneous process and economic evaluations were made on the Johnstone Zinc Oxide process, the new Fluidized Zinc Oxide process, and a Magnesium Base Slurry SO_2 Scrubbing system.

Evaluations involving the Johnstone Zinc Oxide process included an analysis in which sulfur dioxide recovered from the absorbent was converted to sulfur using the Asarco process. If product sulfur could be sold for $20 per long ton, the net cost of operating this SO_2 removal/sulfur recovery process on a 1400 MW power plant (at a 70% load factor) would approximate $1.36 per ton of coal burned. The economics of converting the sulfur dioxide to sulfuric acid (see Volume I) was reevaluated on the basis of lower sales prices for the sulfuric acid produced. An analysis of using reverse osmosis to separate the oxidation product from the absorbent indicated an uneconomical system based on current technology.

The evaluation of the optimized new Fluidized Zinc Oxide process showed relatively low capital and operating costs for a system serving a 1400 MW power plant; however, it must be recognized that this projection is based on the presumed validity of data that has been generated on a very small-scale laboratory equipment.

The cost study of the Magnesia Base Slurry SO_2 Scrubbing system was made only on the absorption system. An evaluation of the regeneration system, which was not available, would have to be made to complete the analysis.

The major conclusions which have been drawn from the work reported in Parts Two to Six of Volume II are the following:

- Efficient absorption of SO_2 at flue gas concentrations can be effected through the use of dry, fluidized basic materials in the range of 50° to $60^\circ C$, if sufficient water is incorporated into the gas phase upstream of sorbent contactor.

- The formation of sulfate can be essentially eliminated in a fluidized bed absorber, and reduced to a very low value in an aqueous absorber, through the use of ferrous ion in an aqueous prescrubber to reduce NO_2 to NO.

- The thermal decomposition of both zinc and magnesium sulfites is markedly promoted by the presence of steam. The use of steam permits the decomposition of zinc sulfite to be carried out at a temperature below that at which disproportionation occurs.

- A new process for the removal of SO_2 from flue gas is described in which dry fluidized zinc oxide is used as the absorbent. The oxide is recovered for reuse upon thermal decomposition of the resulting sulfite, and the liberated SO_2 is recovered as such. Little or no sulfate is formed.

- NO_x (especially NO_2) is the major contributor to oxidation of the sorbent in aqueous solution systems.

- In general, the inhibitors and complexing agents investigated did not lower the level of oxidation in the presence of NO_x in the flue gas.

- The level of oxidation is less in sorbent solutions saturated with an inert salt.

- The efficiency of SO_2 removal from flue gas is not affected by the presence of NO_x.

- The economics of the conceptualized fluidized-bed zinc oxide process appear to be superior to other regenerable processes for the removal of SO_2 from flue gases, but the state of development of this process is in its very early stage.

One, merely tentative, "conclusion" bears mentioning:

- It appears that adding NO_2 to flue gas to obtain an equimolar ratio of NO/NO_2 prior to scrubbing the gas with aqueous sulfite-bisulfite solutions or slurries, for SO_2/NO_x removal will not lower the NO_x content of the gas significantly, but will cause unwanted oxidation of the sulfite to sulfate to increase drastically.

PART TWO

NEW AQUEOUS PROCESSES

I. INTRODUCTION

A major area of interest on the present program has been concerned with the conception of new aqueous processes for the removal of SO_2 from flue gas, and with a demonstration in the laboratory of the feasibility of such processes. The scope of this effort was considered to be broad, in the sense that a candidate process need not require the presence of bulk water to be included in the aqueous category. In particular, the use of dry fluidized zinc oxide as the absorbent, which was briefly investigated earlier in the program (Reference 1) was considered to fall within the scope of the present effort, since the absorption step will not occur in the absence of water vapor. The fact that the envisioned process in this case involves aqueous prescrubbing to remove fly ash and SO_3, and that the absorption of SO_2 is conducted at about 50°C, which is common to all aqueous processes, would further indicate that this type of process should be included in any general study related to aqueous systems.

II. FLUIDIZED ZINC OXIDE AS AN SO_2 ABSORBENT

A. INTRODUCTION

The original concept involving direct absorption of SO_2 onto fluidized zinc oxide was formulated on the original contract on the basis that the reaction of interest represents a simple neutralization of acidic and basic reactants, and that this type of reaction is in general highly dependent upon the presence of water:

$$ZnO + SO_2 + 2\text{-}1/2\ H_2O \xrightarrow{H_2O} ZnSO_3 \cdot 2\text{-}1/2\ H_2O \qquad (1)$$

Whether or not water vapor would suffice to promote Reaction 1 to the desired extent formed the basis for most of the initial experiments on absorption.

Early in the program, consideration was given to the use of an aqueous prescrubber to remove fly ash, and to introduce additional water vapor into the flue gas. In the practical case, a prescrubbed gas should be available for SO_2 removal at about 50°C, and this temperature was therefore employed as the fluidized bed temperature in most of the early work. The experiments to be described were conducted in the manner that had been previously used by the Bureau of Mines in their screening of metal oxides as SO_2 absorbents (Reference 2). Zinc oxide was included in their study, but was found to be inactive at 130°C in the absence of appreciable water vapor.

In addition to the absorption problem per se, it was considered necessary to conduct the absorption step, if possible, in such a manner that little or no oxidation of the SO_2 occurred:

$$ZnSO_3 \cdot 2\text{-}1/2\ H_2O + [O] \longrightarrow ZnSO_4 \cdot H_2O + 1\text{-}1/2\ H_2O \qquad (2)$$

The formation of zinc sulfate is highly undesirable in that this compound is considerably more difficult to convert to the reusable oxide than is zinc sulfite.

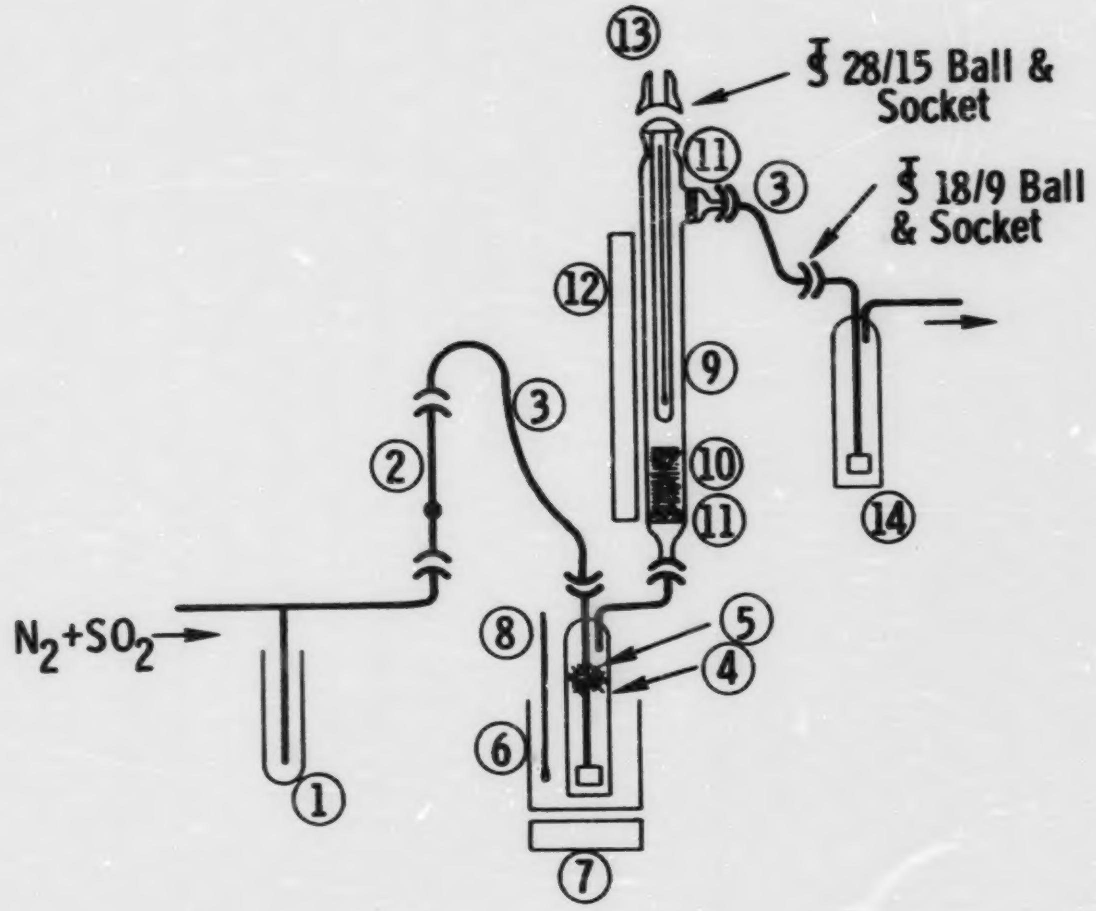
In the following sections the results that were obtained relating to the absorption of SO_2 by fluidized zinc oxide will be presented and discussed.

B. APPARATUS

The absorption apparatus that was originally used on the program is shown in Figure 1. The dry gas was metered at a space velocity of approximately 1050 hr^{-1} into the water sparger, which was maintained at approximately the selected absorption temperature by means of a water bath. Glass wool was placed directly in the sparger unit to prevent the introduction of liquid into the reactor. The upper part of the sparger was wrapped with heating tape, which was extended to include the entire reactor. The reactor was agitated by means of a vibrating table. A thermometer well was fabricated so that the bulb of the inserted thermometer was in the zone just above

Note :

Upper portion of water sparger and entire reactor wrapped with electrical heating tape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$ 28/15 Ball & Socket
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N_2+SO_2
⑧
⑤
④
⑥
①
⑦

① Mercury Bubbler
② Flowmeter
③ Flexible Tubing (Tygon)
④ Water Sparger
⑤ Glass Wool
⑥ Water Bath
⑦ Heater
⑧ Thermometer
⑨ Reactor , 15" Between Frits
(On center) x 1" OD
⑩ Zinc Oxide Bed
⑪ Glass Frit
⑫ Vibrating Table
⑬ Thermometer Well and
Thermometer
⑭ Iodine Sparger

FLUIDIZED BED REACTOR SYSTEM
Figure 1

the surface of the zinc oxide charge, and was therefore continuously bathed with fluidized zinc oxide during a run. Metallic mercury was used for heat transfer in the thermometer well. Unreacted SO_2 in the exiting gas was absorbed in standard 0.1 N iodine, and the excess iodine titrated with standard 0.1 N sodium thiosulfate.

A run was considered to have reached "breakthrough," in conformance with the experimental work conducted by the Bureau of Mines, when an analysis of the iodine solution showed that 10% or more of the influent SO_2 was escaping the bed. In general, the time of breakthrough was sharply defined, in that the absorption of SO_2 was normally complete until breakthrough occurred, at which time the rate of absorption fell rapidly to zero.

Following Run 1, the gas inlet system was modified so that various gas compositions could be introduced into the bed. The overall apparatus (without heating tapes) is shown in Figure 2. The panel board shown in the figure included manometers and flowmeters for the individual gaseous constituents, which included N_2, O_2 (as air), SO_2, CO_2, NO, and NO_2. Other changes made at this time included the insertion of a thermowell directly into the water sparger, and the use of three heating tapes instead of one. The lower tape was used from the upper part of the sparger to the gas inlet to prevent premature water condensation. The second tape was placed around that portion of the absorber that contained the fluidized zinc oxide. The third tape was used to prevent water condensation in the upper part of the absorber.

C. ABSORPTION AND OXIDATION OF SO_2

A total of nine runs were made in the absorber, with progressively complex gas compositions (see Tables 1 and 2). Zinc oxide designated as Kadox-15 (99.6% ZnO), which was obtained from the New Jersey Zinc Company, was used in all of the runs. The initial run was conducted on the previous program, and the results were reported in detail in Volume One of this report. An analysis of the bed material at the completion of this first run was interpreted as indicating that $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ was present to the

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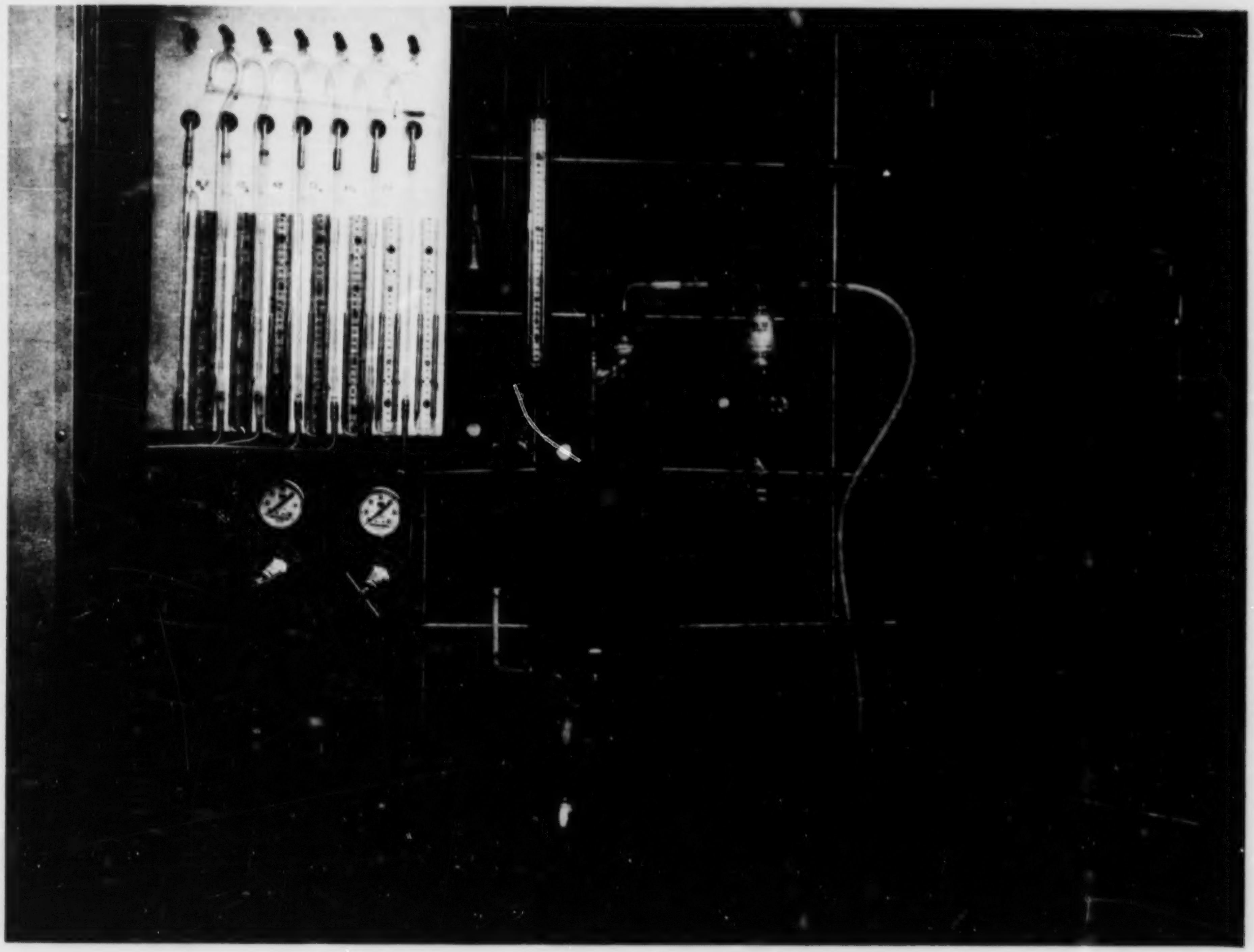


MODIFIED FLUIDIZED BED REACTOR SYSTEM

Figure 2

TABLE 1

REACTION OF FLUIDIZED ZINC OXIDE (60-200 Mesh, Kadox-15), WITH SELECTED FLUE GAS COMPONENTS

(As Depicted in Table 2)

Run No.	Temp. (°C)	Reaction Time (hrs)	SO_2 Absorbed (g/100 g ZnO)	Absorbed SO_2 Converted to Zinc Sulfate (%)	ZnO Converted to $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ (%)
1[a]	35 & 50	15	19.2	2.34	22.0
2[b]	50	27	55.6	0.41	67.6
3[b, c]	50	23	48.1	13.7	49.0
3A	50	23	40.7	13.0	36.8
3B	50	23	52.4	14.2	56.1
4[d]	55	12	24.9	0.32	29.9
5[d]	55	12	24.7	2.65	27.5
6[d]	55	12	22.1	6.55	22.6
7[d, e]	55	12	31.3	4.90	28.6
8[d, e, f]	55	12	31.7	4.72	29.8
9[d, e, g]	55	12	29.9	0.42	28.8

---

[a] This run was conducted at 35° during the first 6-1/3 hours, and carried beyond SO_2 breakthrough which occurred at 9 hours.

[b] Run terminated at SO_2 breakthrough.

[c] Composite of 3A, representing the free-flowing portion of the reaction product, and 3B, which was caked.

[d] Run terminated arbitrarily.

[e] 1% fly ash added to bed.

[f] 5% metallic zinc dust added to bed.

[g] Sparger liquor consisted of 1% iron (as $FeSO_4$) in 5% H_2SO_4.

TABLE 2

GASEOUS COMPOSITIONS AND SPACE VELOCITIES FOR RUNS GIVEN IN TABLE 1

(Total gas flow approximately 600 ml per minute)

Run No.	N_2	SO_2	H_2O	CO_2	O_2	NO	NO_2	Space Velocity (hr^{-1})
	(vol-%)							
1[a]	95.7	0.25	4.01	-	-	-	-	1095
1[b]	93.9	0.25	5.90	-	-	-	-	1118
2	75.8	0.29	9.40	14.3	-	-	-	1122
3	72.0	0.28	11.00	14.1	2.68	-	-	1143
4	72.2	0.28	10.60	14.2	2.68	-	-	1140
5[c]	74.1	0.29	8.20	14.6	2.76	0.058	-	1106
5[d]	70.6	0.28	12.60	13.9	2.63	0.055	-	1161
6	71.5	0.28	11.38	14.1	2.67	0.056	0.005	1147
7	71.9	0.28	11.03	14.1	2.68	0.056	0.005	1141
8	72.0	0.28	10.82	14.1	2.68	0.056	0.005	1138
9	71.9	0.28	11.00	14.1	2.68	0.056	0.005	1141
-[e]	70.9	0.28	12.18	13.9	2.70	0.045	0.005	-

---

[a] At 35°. [b] At 50°. [c] First 7 hours. [d] Last 5 hours.

[e] Theoretical values, based on flue gas leaving aqueous prescrubber at 50°C with 90 percent of the contained NO_x in the form of NO.

extent of 39.7%. It may well be, however, that the basic sulfite, $ZnSO_3 \cdot ZnO$, was actually the major sulfite species formed, especially in view of the limited conversion of zinc oxide to the sulfite. This is suggested by the observed mode of thermal decomposition of the sulfite, which yields the basic sulfite as an intermediate (Reference 3):

$$2\ ZnSO \cdot 2\ 1/2\ H_2O \xrightarrow{\Delta} ZnSO_3 \cdot ZnO + SO_2\uparrow + 5\ H_2O\uparrow \tag{3}$$

$$ZnSO_3 \cdot ZnO \xrightarrow{\Delta} 2\ ZnO + SO_2\uparrow \tag{4}$$

Although the gaseous mixture utilized in the preliminary studies (0.3 vol-% SO_2 in N_2) contained no oxygen, an additional analysis of the bed material following absorption showed that 2.34% of the absorbed SO_2 had been converted to sulfate. Presumably, the formation of sulfate arose from occluded air on the oxide used, and from exposure of the solid to the atmosphere on several occasions during the absorption period.

Beginning with Run 2 the Kadox-15 was screened with standard Tyler screens, and the combined fraction in the range 60 to 200 mesh was used for absorption. The data for Run 1, observed on the previous contract, are included for comparison. In this run absorption fell to 90% in about 9 hours, but the run was nevertheless continued for 15 hours, as discussed in detail in Volume I of this report.

The relatively efficient absorption in Run 2, in which CO_2 was incorporated into the influent gas, is attributed to the increased water content in the gas phase over that present in Run 1, as shown in Table 2. In the practical case the flue gas leaving the prescrubber should be saturated with water vapor at about 50°C, and would then exhibit the following composition:

	Flue Gas (Excluding Fly Ash)	
	Entering Prescrubber (vol-%)	Leaving Prescrubber (vol-%) 50°C
N_2	74.9	70.9
CO_2	14.7	13.9
H_2O	7.25	12.18
O_2	2.8	2.7
SO_2	0.30	0.28
NO_x	0.05	0.05

From the above data it appears that even in Run 2 the influent gas to the fluid bed absorber was not saturated with water vapor. The water sparger was maintained at 50°C for the run, so that presumably the contact time was insufficient to permit the gas to become saturated.

The fact that rather extensive absorption occurred in Run 2 indicates that either zinc carbonate does not form, or that if formed it reacts readily with SO_2 to displace CO_2. Some caking of the solid in the lower portion of the absorption bed was noted at the conclusion of the run, but most of the solid remained highly fluid throughout the run. Screening of the solid showed that little or no attrition occurred during the 27 hour absorption period:

Mesh Size	Reactant Kadox-15 (wt-%)	Product of Run 2 (wt-%)
Over 60	-	1.7
60 to 100	52.1	53.3
100 to 150	24.3	23.0
150 to 200	23.6	19.3
Under 200	-	2.7

Run 3 represents the first run in which oxygen was incorporated into the gas phase. The run was complicated by the appearance of liquid water in the bed, and this resulted in partial defluidization. Probably for this reason breakthrough (>10 percent of the influent SO_2 escapes in the exit gas) occurred before the 27 hours realized in Run 2. The presence of water in the bed is attributed to the relatively high water content in Run 3 (11 vol-% of the influent gas), which corresponds to a nearly saturated gas (12.18%, see Table 2) at the bed temperature of 50°C. It may be presumed that either temperature fluctuations within the bed resulted in the condensation of water from time to time, or that the zinc sulfate formed was deliquescent under the conditions employed. In the latter case, the process of water condensation would be further promoted by the fact that liquid water aids in the further formation of sulfate. This is indicated by the dramatic decrease in sulfate content which occurred in Run 4, which was carried out at 55°C, and in which no water condensation occurred.

At the conclusion of Run 3, only the top 20 vol-% of the bed material was fluid enough to be poured from the tube; the remainder was loosened with a spatula and dried overnight in a stream of nitrogen. The water lost in this manner represented 31 wt-% of the total bed material after absorption. The dry solid was then removed and ground in a mortar prior to analysis. Separate analyses of the fluid portion and residual portion of the bed material are shown in Table 1 as 3A and 3B, respectively. The sulfate content was approximately the same in both samples, but the sulfite was located largely in the defluidized or lower portion of the bed. This is probably to be attributed to the insolubility of the sulfite, which remained at the site of formation once the bed had defluidized, whereas the soluble sulfate would tend to migrate as a result of digestion (solution followed by precipitation).

In Run 4 the formation of liquid water in the bed was prevented by raising the bed temperature to 55°C, while maintaining the sparger temperature at 50°C. The higher bed temperature could probably be realized in the practical case through adjustment of the amount of heat removed, if any, from the hot regenerated zinc oxide before returning it to the absorber, by taking advantage of the exothermic nature of Reaction 1, or by providing an external source of heat. Because of the relatively long absorption periods required for breakthrough in Runs 2 and 3, it was decided to conduct subsequent runs for an arbitrarily selected 12 hours. This time period is sufficient for a degree of absorption commensurate with reasonable accuracy in the analytical values shown in the table.

As can be seen from a comparison of Runs 3 and 4, a remarkable reduction in sulfate formation occurred when the gas was maintained above its dew point. The bed material from Run 4 was completely free-flowing.

In Run 5, NO was incorporated into the gas, with the result that an increase in sulfate formation occurred. It is not known whether the NO reacted primarily as such in causing the formation of sulfate, or whether it was first partially oxidized to NO_2 by the oxygen present in the gas. If it is assumed that no oxidation of NO occurred, it was calculated that 36.8% of the available NO would be utilized in sulfate formation, according to the following equation:

$$2\,NO + ZnSO_3 \cdot 2\text{-}1/2\ H_2O \longrightarrow N_2O + ZnSO_4 \cdot H_2O + 1\text{-}1/2\ H_2O \qquad (5)$$

If only NO_2 were involved, it would require that 18.4% of the NO be oxidized:

$$NO_2 + ZnSO_3 \cdot 2\text{-}1/2\ H_2O \longrightarrow NO + ZnSO_4 \cdot H_20 + 1\text{-}1/2\ H_2O \qquad (6)$$

These alternatives can be distinguished by utilizing a gas containing NO, but no oxygen.

In Run 6, NO_2 was included in the gas, to the extent that 10% of the NO_x consisted of NO_2. Oxidation was somewhat more extensive in this case, as noted in the table. If it is assumed that no oxidation of NO to NO_2 occurred, it appears that the action of NO_2 is a catalytic one in the sense that 3.6 sulfate moieties were formed for each NO_2 molecule present. This could arise as a result of Reaction 6, in which the NO_2 is destroyed (non-catalytic) together with a reaction involving the formation of an activated NO_2-oxygen complex (catalytic):

$$NO_2 \cdot + \cdot O_2 \cdot \longrightarrow \left[O_2N\text{-}O_2 \cdot\right] \qquad (7)$$

$$\left[O_2N\text{-}O_2 \cdot\right] + 2\,SO_3^{=} \longrightarrow NO_2 \cdot + 2\,SO_4^{=} \qquad (8)$$

Reaction 7 is considered reasonable in view of the diradical nature of the oxygen molecule, and the tendency of NO_2 to dimerize. Since the free radical NO does not dimerize, its tendency to form a complex analogous to that shown in Reaction 7 would be considerably less. The occurrence of a catalytic process, such as that shown in Reactions 7 and 8, can be distinguished from non-catalytic oxidation, involving pre-oxidation of NO to NO_2 followed by oxidation of sulfite via Reaction 6, by utilizing NO_2 in the gas phase in the absence of NO.

In Run 7, fly ash was present in the bed for the first time. Inasmuch as an efficient prescrubber did not form part of the experimental apparatus, it was not possible at this time to introduce the ash directly into the feed gas, remove the bulk of the ash by prescrubbing, and then conduct the gas containing residual ash into the bed. Instead, ash was introduced (1% of the bed weight) directly into the bed, and thoroughly mixed by fluidization of the bed with nitrogen before admission of the flue gas. This amount of ash represents approximately 6.5 times the amount which would be expected to enter the bed if the prescrubber were 99% efficient in removing the ash, and if the fluidized bed run had been conducted to breakthrough (i.e., the point at which 10% or more of the SO_2 passes completely through the bed).

The presence of fly ash in the bed did not result in increased oxidation. This can be explained on the basis that no leaching of iron oxide from the ash occurs in the absence of a bulk liquid phase, and that the oxidation of zinc sulfite by oxygen is very slow in the absence of heavy metal ions (e.g., ferric ion) as catalysts. Consequently, the need does not arise in the case of a fluidized zinc oxide absorber for the use of inhibitors, such as hydroquinone, as antioxidants.

It will be noted from Tables 1 and 2 that only 0.32% oxidation occurred in the fluidized bed system for a gaseous mixture containing O_2 but no NO_x (Run 4), and it is therefore inferred that the oxidation in Run 7 is attributable to the presence of NO_x in the gas. On this basis, Run 8 was conducted with metallic zinc incorporated into the bed. In aqueous solutions of SO_2, sulfites are reduced by zinc dust to give dithionite ion, $S_2O_4^{=}$, which acts as a very strong reducing agent (Reference 4).

$$Zn + ZnSO_3 \cdot 2\text{-}1/2\ H_2O + SO_2 \xrightarrow{H_2O} ZnS_2O_4 + ZnO + 2\text{-}1/2\ H_2O \tag{9}$$

$$ZnO + SO_2 + 2\text{-}1/2\ H_2O \xrightarrow{H_2O} ZnSO_3 \cdot 2\text{-}1/2\ H_2O \tag{1}$$

If water vapor were to promote Reaction 9, the zinc dithionite formed might then effectively reduce the undesired NO_x to NO and/or N_2O, which would be less effective in oxidizing sulfite to sulfate:

$$ZnS_2O_4 + NO_2 \longrightarrow ZnSO_3 + SO_2\uparrow + NO\uparrow \tag{10}$$

$$ZnS_2O_4 + 2\ NO \longrightarrow ZnSO_3 + SO_2\uparrow + N_2O\uparrow \tag{11}$$

It was found, however, that Reaction 9 does not occur in the absence of liquid water. Evidence for this conclusion was obtained on noting that the addition of a sample of the bed material to acid, following the completion of Run 8, gave no precipitate of free sulfur. The formation of sulfur in this manner is characteristic of the decomposition of dithionites:

$$2\ ZnS_2O_4 + 3\text{-}1/2\ H_2O \xrightarrow{H^+} Zn(HSO_3)_2 + ZnSO_3 \cdot 2\text{-}1/2\ H_2O + S\downarrow \tag{12}$$

Run 8 may therefore be considered as a duplicate of Run 7, and it will be noted from Table 1 that the results for these two runs are largely in agreement. An interesting observation that was made in connection with Run 8 was that during the course of the run the zinc metal tended to accumulate in the upper part of the tube. At the end of the run most of the gray metal had separated in this manner. The residual bed material (60-200 mesh) was nearly white, although speckled with fly ash. Apparently the small particle size of the metal (about 4 microns) counteracted its relatively high density (Zn, 7.14 g/cc; ZnO, 5.47 g/cc).

Run 9 represents what is considered to be the ultimate solution to the oxidation problem in the zinc oxide fluidized bed system. As a result of a series of experiments involving the oxidation of iodide ion by NO_x, which will be discussed below in some detail, Run 9 was conducted with ferrous sulfate present in the sparger. Under these conditions NO_2 is reduced to NO (Reference 5):

$$2\ FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO \qquad (13)$$

Fortunately, the oxidation of ferrous ion by oxygen is inhibited by the presence of sulfuric acid (Reference 6), so that loss of ferrous ion due to this undesired oxidation reaction is not appreciable.

In the practical case, the sulfuric acid required for Reaction 13 would be provided to the prescrubber by the SO_3 content of the incoming flue gas, and the ferrous sulfate through the use of scrap iron:

$$Fe + Fe_2(SO_4)_3 \longrightarrow 3\ FeSO_4 \qquad (14)$$

However, the iron needed for effecting Reaction 14 would not be added directly to the prescrubber, inasmuch as additional experiments have shown that SO_2 is partially reduced to free sulfur by the direct action of metallic iron in acid solution. Rather, the iron would be located in a recirculating side stream, so that only ferrous iron would be fed to the prescrubber proper. The optimization of this system will require additional experiments.

The experiments which ultimately led to the use of ferrous ion in the sparger are shown in Table 3. The main purpose of these experiments was to determine the relative activity as oxidizing agents of the three oxidizing components of flue gas; i.e., NO, NO_2, and O_2. This could have been

TABLE 3

OXIDATION OF AQUEOUS IODIDE ION BY SELECTED FLUE GAS COMPONENTS UNDER VARIOUS CONDITIONS

Run No.[a]	Gas Components[b]	I_2 Formed (ml $Na_2S_2O_3$)[c]	Reduction of Gas (%)
1[d]	O_2	0.00	0.00
2[d]	NO	0.32	5.25
3[d]	NO_2	1.32	97.4
4[d]	$NO + O_2$	0.41	-
5[d]	$NO_2 + O_2$	1.40	-
6[d]	$NO_2 + NO$	1.80	-
7[d]	$NO_2 + NO + O_2$	1.87	-
8[e]	$NO + O_2$	0.58	-
9[f]	$NO + O_2$	0.58	-
10[f, g]	NO	0.06	81.0
11[f, g]	NO_2	0.11	91.0
12[f, g]	$NO_2 + NO + O_2$	0.25	87.0[i]
13[f, h]	$NO_2 + NO \div O_2$	0.75	60.0[i]

---

[a] Each run was conducted at room temperature for a duration of one hour.

[b] Whenever O_2 was present it constituted 2.68 vol-% of the gas; NO, 0.056%; and NO_2, 0.005%. The diluent was always N_2, with the total flow maintained at 600 ml/min (cf. Table 2).

[c] The I_2 was formed in a bubbler which, for each run, contained 250 ml of a stock solution prepared from 4.4 g of 47% HI and 320 g of KI diluted to 4 liters with water. The I_2 was determined by titration with standard 0.1107 N $Na_2S_2O_3$ to the starch endpoint.

[d] In this run the I_2 bubbler was located at the position normally occupied by the water sparger during a fluidized bed run (see Figure 1).

TABLE 3 (continued)

FOOTNOTES - continued:

[e] In this run a water sparger was located at the normal position used during a run, with the I_2 bubbler immediately downstream.

[f] In this run both the sparger and bubbler were located in their normal positions (i.e., sparger upstream of the fluid bed and the I_2 bubbler downstream).

[g] In this run the sparger contained 1% Fe in 5% H_2SO_4.

[h] In this run the sparger contained 1% Fe in 1% H_2SO_4.

[i] Based on NO + NO_2 content only.

done by contacting the gases with solutions of sulfites, and noting the amounts of sulfate formed under various conditions. However, even the relatively simple turbidimetric method of analysis for sulfate is tedious for large numbers of samples, and moreover is subject to a relatively large (5%) experimental error.

The approach taken to the problem at hand consisted in utilizing aqueous acid solutions of iodide ion as an indicator for the relative activities of the various oxidizing gases. One advantage of this system was that an immediate color change occurred (formation of iodine) if oxidation occurred. Equally important, the liberated iodine could be rapidly and accurately determined by titration with standard thiosulfate solution to the starch endpoint.

The experimental conditions used in carrying out the various runs shown in Table 3 are largely given in the footnotes to the table. In Runs 1 to 3 the water sparger that would normally have been used in carrying out the runs shown in Table 1 was replaced by the iodide bubbler, with no apparatus downstream of the bubbler. The results of these runs show that oxygen alone is relatively ineffective as an oxidant, although the stock solution (see Footnote c of the table) slowly became slightly yellow in color (liberation of iodine) on standing, due to the presence of dissolved oxygen. This required several days, in contrast to the one-hour period utilized for each of the runs. From Run 2 it would appear that NO slowly oxidizes iodide ion. However, further experimental results, discussed below, indicate that the observed oxidation may rather be attributable to NO_2, formed from NO and dissolved O_2, and that this reaction is actually promoted by the presence of liquid water. The extent of reduction of NO_2 (Run 3) is especially noteworthy.

Runs 4 to 7 show that an enhancement of oxidizing power occurs when at least two of the three oxidizing gases are present simultaneously. In Run 4, for example, the observed value of 0.41 is larger by 0.09 than the sum of the results obtained from Runs 1 and 2. If such an enhancement is assumed to operate chiefly on the less (or least) active oxidant, rather than mutually, Run 4 would then be interpreted as showing an enhancement for oxygen of 0.09. In the same manner, Run 5 shows an enhancement for oxygen of 0.08, Run 6 shows 0.16 for NO, and Run 7 shows as one possibility 0.08 for O_2 and 0.15 for NO. The observed enhanced activity can be explained as resulting from the formation of complexes, such as $ON\text{-}O_2\cdot$, N_2O_3, and $O_2N\text{-}O_2$. However, in the case of Run 4 a more probable explanation is that NO_2 formation occurs rather than complex formation. It will be noted that the enhancement of NO is approximately twice that of O_2.

Run 8 is interesting in that the inclusion of a water sparger into the system upstream of the bubbler results in a further increase in the oxidizing capacity of the gas (0.58 for Run 8 vs 0.41 for Run 4). This is interpreted (compare the above paragraph) as indicating that the formation of NO_2 is promoted by the presence of liquid water. That a similar promotion does not occur in the presence of water vapor is shown by Run 9, in which the fluidized bed reactor was interposed between the sparger and bubbler.

In Runs 10 to 12 the sparger contained 5% sulfuric acid, and therefore more closely approximated a true prescrubber liquor composition than does pure water, since flue gas normally contains a small amount of SO_3. Powdered iron was added to the sparger just before each run, and hydrogen was slowly liberated during the run with the formation of ferrous sulfate:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow \qquad (15)$$

As can be seen from the table, a dramatic decrease in oxidizing capacity of the gas entering the bubbler occurred in each case. The effect was somewhat less when a 1% sulfuric acid solution was used (Run 13).

The direct use of metallic iron in the sparger was subsequently found to result in the partial reduction of SO_2 to elemental sulfur, as previously noted, and for this reason an additional experiment (not shown in Table 3) was conducted in order to establish the approximate sparger conditions to be used in Run 9 of Table 1. In this experiment a 1% solution of ferrous sulfate was prepared by allowing metallic iron to react with 5% sulfuric acid (Reaction 15) until all of the iron was consumed. The resulting clear and colorless solution was then heated to the normal sparger temperature of 50°C, the bubbler was placed immediately downstream of the sparger in the manner of Run 8, Table 3, and a mixture of NO_2, NO, and O_2 in the proportions used in Runs 7, 12, and 13, Table 3, was passed through the system at 600 ml per hour. A heating tape was used to prevent water condensation between the sparger and bubbler. The following results were obtained, in terms of ml $Na_2S_2O_3$ required for titration of the liberated iodine after the times indicated: 1st hour, 0; 2nd, 0.09; 3rd, 0.06; 4th, 0.08; 5th, 0.05; 6th, 0.16; 7th, 0.30; 8th, 0.28. These results indicate that the incorporation of ferrous sulfate into the sparger should be highly effective in diminishing the oxidizing capacity of the gas exiting from the sparger, particularly if fresh solution were used after about the fifth hour of the run. In carrying out Run 9 of Table 1, the solution was replaced after the sixth hour.

That oxygen did not oxidize ferrous ion at an appreciable rate under the conditions employed in the experiment described above was shown by noting that if all of the available oxygen had reacted, 10 ml of $Na_2S_2O_3$ would have been required for titration of the liberated iodine after only 4.9 minutes.

The main conclusions to be derived from the data in Tables 1 and 2 are as follows:

- For a gas nearly saturated with water at 50°C, more than 50 g of SO_2 is absorbed per 100 g of zinc oxide before breakthrough occurs.
- If liquid water is permitted to condense in the bed, extensive oxidation results. In the worst case, approximately 14% of the absorbed SO_2 was converted to sulfate (Reaction 2) under conditions such that 31% of the total weight of the bed following absorption consisted of condensed water. Bed defluidization also occurs.

- Oxygen does not cause appreciable oxidation in the absence of a condensed phase. It was found, for example, that with a sparger temperature of 50°C and with the bed maintained at 55°C to prevent water condensation, the inclusion of oxygen in the gas resulted in only 0.32% of the absorbed SO_2 being converted to sulfate.
- The presence of fly ash in the bed does not promote oxidation.
- The presence of NO_2 promotes oxidation, but this component of the gas can be removed in the pre-scrubber through the use of ferrous ion.

It will be noted from Tables 1 and 2 that the observed extent of oxidation for Run 2 (no oxidizing component), Run 4 (oxygen present), and Run 9 (fly ash and all flue gas components present) was in all cases approximately the same (0.3-0.4%). This would suggest that in all probability no oxidation at all occurred in any of these runs. The small percentages of oxidation reported were based on experimental turbidimetric readings of 2 to 3 ppm of sulfate on a scale ranging from 0 to 300 ppm, so that in all cases the readings were within the range of experimental error.

D. ABSORPTION OF NO_x

The bed materials from the various runs described above have been stored for future studies in which it could be determined whether or not NO_x had been absorbed. No work was done in this area on this program. The experiments of interest involve the thermal decomposition of samples of the bed materials, and the collection, identification, and analysis of the liberated gases. If NO_x has been absorbed, various nitrogen oxides should be evolved on heating, perhaps at relatively low temperatures.

III. ZINC OXIDE PARTICLE SIZE AND ACTIVITY

A. INTRODUCTION

The initial work during Phase IV was in part directed to the problem of particle size degradation in connection with the use of zinc oxide as a fluidized absorbent for SO_2. Earlier results (Reference 1) indicated that the absorption step is highly dependent on particle size, and that extremely small particles are required for good absorption. In particular, New Jersey Zinc's Kadox-15, of 0.1 μ mean particle size, was much more effective than their XX-504, of 99.6% purity and 1.5 μ. The use of such small particles is considered to be highly undesirable, both because of the inevitable loss of solids by entrainment from the bed, and because the calcination of zinc sulfite, as studied extensively by Johnstone and Singh (Reference 7), does not yield an oxide of such a small particle size for reuse in the bed. In general, the calcination of the sulfite at 450° to 775°C yields material exhibiting particle sizes in the range of 60 to 270 mesh, or 250 μ to 53 μ, respectively. Even this material, however, is undesirably small. Recent studies have shown that it should be possible to utilize relatively coarse material (1/16 in. to 1/8 in. pellets) for absorption.

B. SMALL PARTICLE STUDIES (Kadox-15)

Although Kadox-15 has been found, by microscopic examination, to exhibit a mean particle size of 0.1 μ (data provided by the New Jersey Zinc Company), it was found that agglomeration of the particles readily occurs, so that in fact a much larger particle size is realized. An analysis of Kadox-15 with standard Tyler screens gave the following results:

Mesh Size	Wt-%
Over 65	1.6
65 to 100	21.1
100 to 150	18.0
150 to 200	19.2
Under 200	40.1
	100.0

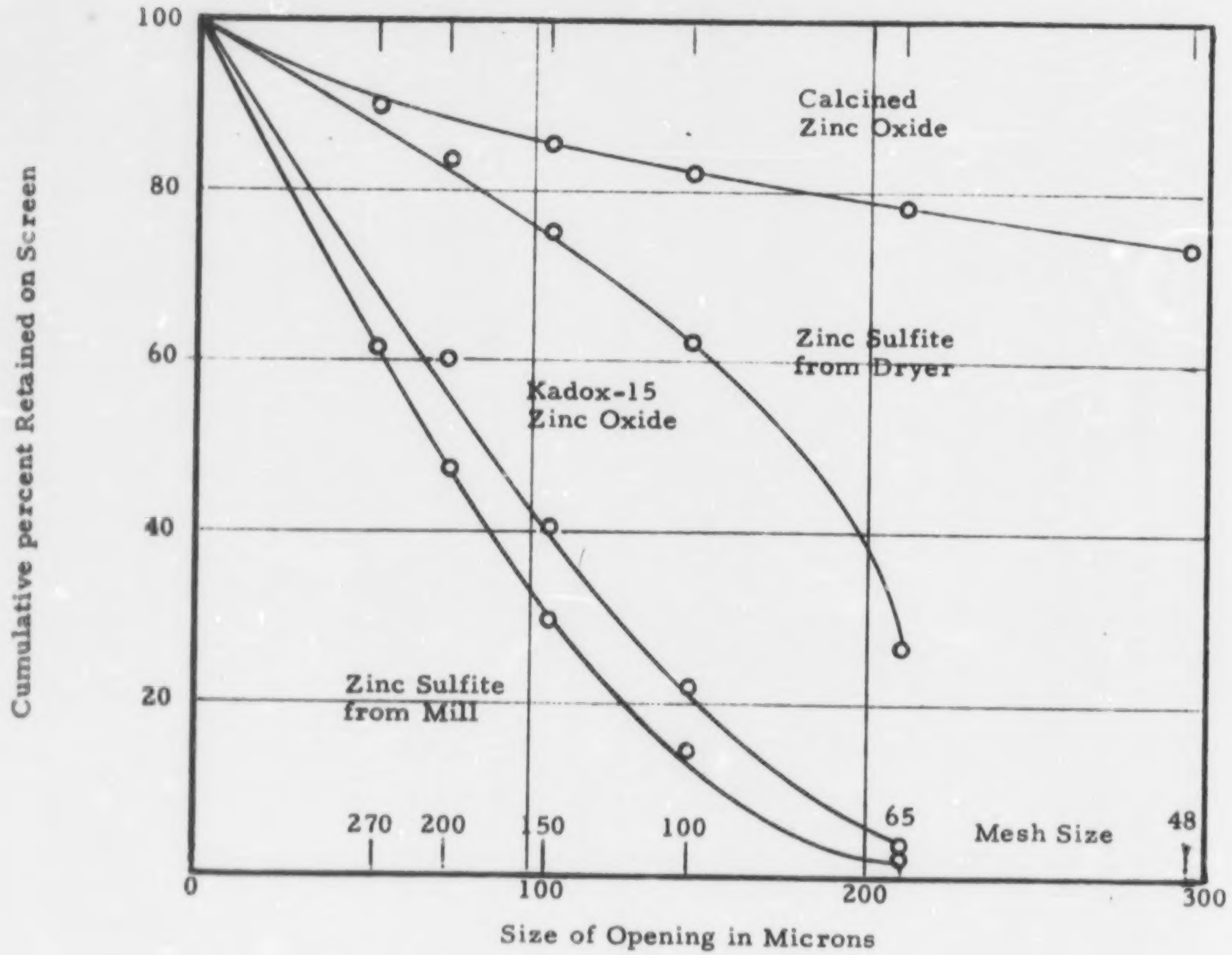
In view of the above analysis the New Jersey Zinc Company was consulted, with the only comment of interest being that a relatively high humidity would be expected to contribute to the agglomeration of the oxide. However, the material was stored in a closed plastic bag which was in turn contained in a metal can, and the screen analysis was carried out under conditions of low humidity. It would appear, therefore, that the material inherently tends to agglomerate, and that earlier work at Aerojet with fluidized Kadox-15 (Table 1, Run 1) involved particle sizes in the ranges noted above, particularly in view of the fact that the gas entering the bed had been passed through a water sparger.

Although the effective particle size of Kadox-15 is much larger than had been supposed, it is somewhat smaller than that used by Johnstone and Singh in their sodium scrubbing/zinc oxide process for the removal of SO_2 from flue gas (Reference 7). Figure 3 shows a screen analysis of dried zinc sulfite, as employed by Johnstone, of the same material after it had been passed through a small hammermill, and of the zinc oxide resulting from the calcination of the sulfite. Kadox-15, which has been included for comparison, shows roughly the same range of particle sizes as that of Johnstone's milled sulfite. It is of interest that an increase in particle size occurs when the sulfite is calcined, even though the process is a degradative one, involving the loss of both water and SO_2. This further attests to the tendency of zinc oxide to agglomerate, and indicates that any particle attrition which occurs during the absorption of SO_2 by fluidized zinc oxide may be effectively offset on calcining the resulting sulfite.

The zinc oxide obtained on calcination of the sulfite was described by Johnstone as being highly active in the sense that it dissolved in a specially prepared aqueous solution of sodium sulfite-sodium bisulfite in a "few seconds." The particular medium chosen for dissolution of the oxide closely approximates the spent scrubber liquor obtained in the Johnstone Zinc Oxide process. The regeneration step in this process involves the conversion of bisulfite to sulfite through the use of the oxide:

$$2\,NaHSO_3 + ZnO + 1\text{-}1/2\,H_2O \longrightarrow ZnSO_3\cdot 2\text{-}1/2\,H_2O\downarrow + Na_2SO_3 \qquad (16)$$

(Data from Johnstone, Reference 7, except for Kadox-15)



SCREEN ANALYSIS OF ZINC SULFITE AND ZINC OXIDE

Figure 3

The zinc sulfite obtained in Reaction 16 is calcined to regenerate the oxide, and the sodium sulfite solution is returned to the scrubber. In the case of Kadox-15, which is of smaller particle size than Johnstone's calcined oxide, it was found by Aerojet that solution in the particular sulfite-bisulfite medium of interest required at least two minutes, and that a small amount of material had failed to dissolve during ten minutes, at which time the sulfite began to precipitate in accordance with Reaction 16. This phenomenon was considered of sufficient interest to warrant a further brief study.

The results of a series of qualitative tests involving the solution of a variety of zinc oxide samples in aqueous sodium sulfite-sodium bisulfite are shown in Table 4. In order to determine whether magnesium and/or calcium might be substituted for zinc in the Johnstone Zinc Oxide process, basic compounds of these elements were also included in the study. With respect to this point it was found that magnesium might be substituted for zinc, but that calcium is unsuitable in that the hydroxide does not dissolve. Since the medium used was acidic (pH approximately 5.5) the surface of the hydroxide must have reacted, but the rate of formation of calcium sulfite on the hydroxide surface was apparently rapid enough to prevent appreciable solution of the hydroxide. The use of magnesium in the Johnstone process is desirable from an economic standpoint, but was not further investigated, pending preliminary results relating to the possible elimination of the disproportionation reaction when magnesium sulfite is calcined.

The results shown for zinc oxide are interesting in that they clearly indicate that calcination greatly improves the ability of the oxide to dissolve. Since the solution of the oxide is accomplished in an aqueous medium, the heating of the oxide in the present study must involve the loss of one or more surface contaminants other than water. It may also be noted from the data that small particle size favors solution of the oxide, and that heated material of small particle size gave the best results, that is, rapid and complete solution.

TABLE 4

RATE OF SOLUTION OF SELECTED METALLIC OXIDES AND HYDROXIDES IN AQUEOUS SODIUM SULFITE-SODIUM BISULFITE SOLUTION

$C^{*} = 3.00$, $S^{**} = 2.50$, $S/C = 0.83$

Oxide or Hydroxide added = 3/8 mole per mole of $NaHSO_3$

Material Added	Time Required for Dissolution of Solid (min)	Remarks
ZnO, Kadox-15	2	a
same, over 32 mesh	2	a
same, 65 to 100 mesh	1	b
same, under 200 mesh	1	b
same, under 300 mesh	3/4	b
same, calcined[j]	1/2	c
same, under 200 mesh, calcined[j]	1/2	d
same, under 300 mesh, calcined[j]	1/2	d
ZnO, XX-504	4	a, f
ZnO, Allied Chemical	2	b
same, calcined[j]	1 1/2	c
$Zn(OH)_2$	1 1/2	b, f
Calcined $ZnSO_3 \cdot 2\ 1/2H_2O$	3/4	d
MgO	1 3/4	c, g
$Mg(OH)_2$	1/2	d, e, g
$Ca(OH)_2$	-	e, h

---

[a] Solution moderately hazy

[b] Solution slightly hazy

[c] Solution very slightly hazy

[d] Solution clear

[e] Solution slightly yellow

[f] Solution very slightly yellow

[g] Precipitate began to form in about 2 min; heavy crystalline precipitate in 20 min.

[h] Solid did not dissolve.

[j] Heated at 550°C for 2 hrs.

[*] moles of Na per 100 moles of water.

[**] moles of SO_2 per 100 moles of water.

In summary, it may be stated that the overall results of Table 4 are considered significant in indicating that magnesium, but not calcium, might be substituted for zinc in the Johnstone Zinc Oxide process, and that calcined zinc oxide might be a better absorber for SO_2 in a fluidized bed application than zinc oxide which has been exposed to air for an appreciable length of time (if, in fact, the rate of dissolution of zinc oxide in aqueous media is a measure of its ability to sorb SO_2).

C. LARGE PARTICLE STUDIES (Pelleted Kadox-215)

1. Introduction

In addition to the studies described above relating to Kadox-15, a brief experimental program was conducted in which it was shown that considerably larger particles could be used for absorption, and that under the proper experimental conditions very little particle attrition occurred.

2. Initial Fluidization Experiments

All of the experiments described below were conducted with 1/16 - 1/8 in. particles, and at superficial gas velocities in the range of 2.7 to 3.0 fps. The fluidization tube, 15 in. x 7/8 in. ID, was that designated as Item 9 in Figure 1. Air was used for fluidization.

Initial experiments were conducted with 30 g samples of New Jersey Zinc's pelleted zinc oxide, Kadox-215, and with suitably screened commercially available zinc sulfite. Considerable attrition occurred in the case of the oxide during a two-hour fluidization period, with only 33% of the final material retained on a 10 mesh (1/16 in.) screen. Of the material passing the screen, 37% was retained on a 60 mesh screen. On the other hand, zinc sulfite was highly resistant to attrition. After two hours, the following screen analysis was obtained:

Mesh Size	Wt-%
+ 10	97.2
- 10 + 24	2.3
- 24	0.5
	100.0

Subsequent experiments involved zinc oxide derived from the calcination of the commercial sulfite at 275°C. Although this material was friable, it possessed sufficient mechanical strength to permit fluidization without observable attrition during the 1-hour test period employed. When mixed with zinc sulfite, the fluidized mass readily separated into two solid phases, with the oxide appearing as the upper phase. Overall, the calcined oxide was found to be much more resistant to attrition than the commercially pelleted Kadox-215.

Another experiment with the calcined oxide involved a preliminary absorption of sulfur dioxide (from gaseous SO_2-N_2-H_2O) prior to fluidization. The purpose of this experiment was to determine the resistance of sulfite-coated oxide to attrition. The coating process was arbitrarily terminated after 15% of the theoretical amount of sulfur dioxide had been absorbed. Subsequent fluidization with air at 2.7 fps for one hour resulted in material which exhibited the following screen analysis:

Mesh Size	Wt-%
+ 10	97.2
+ 10 - 24	6.2
- 24	1.8
	100.0

3. Attrition During Absorption of SO_2 in a Fluidized System

a. Apparatus

A fluidized bed absorption system was improvised, largely from equipment that had been used in studies relating to the oxidation of Na_2SO_3-$NaHSO_3$ solutions. The resulting system was not considered adequate for long-term experimentation, but did serve to provide basic fluidized bed attrition and absorption data.

A mixture of N_2 and SO_2 was saturated with water at 45-50°C in a packed column. The saturated gas flowed to a fluidized bed absorber made from 43 mm ID glass tubing. A coarse glass frit was used as a fluidizing plate and a 300 mesh screen served as an outlet filter on the absorber. Zinc oxide was slug fed at an approximate rate of 1 g/min (later at 1 g/2 min). The reacted absorbent was continuously withdrawn through a glass overflow tube positioned 3 inches above the fluidizing plate in the initial tests. The tube was later raised to 6 inches above the plate. The fluidized bed and the water-saturated gas upstream of the saturator were maintained at temperatures in excess of 55°C in order to prevent water condensation in the system.

A muffle furnace was used to regenerate zinc oxide from zinc sulfite formed from the oxide in the absorber. The sulfite was placed in Petri dishes and decomposed at 350-425°C while the furnace was purged with nitrogen.

b. Experimental Work

Table 5 shows the results of the attrition tests. Kadox-215 zinc oxide pellets were used in Run 1 with a particle size of 50% -12+16 mesh and 50% -16+24 mesh. The bulk density of this mixture was 1.1 g/ml (68.6 lb/ft^3). An initial charge of 90 g was placed in the absorber and was then soaked for 3 hours with a water-saturated mixture of N_2 and SO_2, fed at a rate of 26 liters/min N_2 and 360 ml/min SO_2. After soaking, the absorbent analyzed 18.4 wt-% SO_2. The particles partially converted to zinc sulfite in the absorber were hard and firm, whereas the unreacted feed pellets were soft and could be pulverized with finger pressure. It was observed that a small increase in pellet diameter occurred during absorption.

In Run 1 the unreacted, relatively soft zinc oxide pellets were fed at a rate of about 1 g/min. The absorbent overflow was set at 3 inches above the fluidizing plate. A mixture of 50°C-saturated gas at a rate of 60 liters/min N_2 and 280 ml/min SO_2 (0.47% SO_2) was fed to the absorber. The feed rate was equivalent to a superficial velocity of 2.86 fps.

TABLE 5

ATTRITION EXPERIMENTS DURING SO_2 ABSORPTION

	Run No. 1 (Using As-Received ZnO Pellets)				Run No. 2 (Using Regenerated ZnO Pellets)						
	Time, Hr.				Time, Hr.						
	0	1	2	2.5	0	1	2	2.5	3.5	4.5	5.5
Fluid, Bed-Depth, in.	3	3	3	3	3	3	3	3	6	6	6
ZnO Feed, ≈ g/min	1	1	1	1	1	1	1	1	1	1	0.5
ZnO Residence Time, hr	-	0.92	0.90	0.82	-	0.89	0.84	1.4	-	1.8	3.1
Product Rate, g/hr	-	81.9	83.8	91.8	-	84.5	89.6	52.6	74.0	71.8	42.3
Feed Rate*, g/hr	-	60.6	65.8	72.4	-	70.8	80.1	47.0	-	62.5	36.9
Product Sieve Analysis, wt-%:											
+12 mesh	-	0.1	0.4	0.4	-	0.2	0.3	0.1	-	0.3	0.2
-12+16 mesh	50	36.0	38.2	32.5	50.0	46.2	42.4	37.1	-	43.0	43.6
-16+24 mesh	50	57.3	53.1	56.1	50.0	49.3	53.0	58.3	-	52.9	51.7
-24 mesh	-	6.6	-	-	-	-	-	-	-	-	-
-24+60 mesh	-	-	8.2	10.9	-	4.3	4.3	4.4	-	3.8	4.4
-60+100 mesh	-	-	0.09	0.1	-	0.01	0.02	0.02	-	0.04	0.06
-100 mesh	-	-	0.01	0.02	-	0.006	0.003	0.004	-	0.004	0.01

*Calculated from weighed product.

Fluidized bed temperature was in the range of 63-70°C.

Product left in bed after Run 2 with 6" high overflow = 130.8 g.

+300 mesh on outlet screen after completion of run = 0.078 g (< .02% of total product in 5.5 hours).

In Run 2, the absorbent feed was prepared as follows: Kadox-215, of the same particle size distribution that was used in Run 1, was soaked as a static bed for several hours in a mixture of N_2-SO_2-H_2O. These pellets had a bulk density of 1.44 g/ml (90 lb/ft^3), and were hard and firm. The pellets were subsequently decomposed by heating to 425°C for an hour in shallow Petri dishes. The material did not go through a noticeable plastic state, and did not flow into an agglomerated mass. Practically all of the regenerated pellets retained their original shape and were quite firm (much firmer than the original Kadox-215 zinc oxide pellets but softer than the zinc sulfite pellets). About 4 wt-% of the pellets puffed up to almost three times the original diameter and were easily pulverized with finger pressure. It is quite possible that presence of free water caused the change in physical characteristics. Analysis of both types of regenerated pellets showed 0 wt-% SO_2. The bulk density of the regenerated pellets was 1.14 g/ml (71.0 lb/ft^3).

An initial charge of 90 g of regenerated Kadox-215 with a particle size of 50% -12+16 mesh and 50% -16+24 mesh was soaked with N_2-SO_2-H_2O for about an hour in a static bed. After soaking, the absorbent analyzed 11.9 wt-% SO_2. The bed was then fluidized and regenerated zinc oxide pellets were fed at a rate of about 1 g/min. The gas rate was 60 liters/min N_2 and 180 ml/min SO_2, equivalent to 2.86 fps superficial velocity. Table 5 shows the data for Runs 1 and 2.

The primary purpose of these tests was to determine the feasibility of using commercially available zinc oxide pellets for absorption of SO_2 in a fluidized bed. Of particular interest was an indication of the extent of attrition that could be expected. Although some absorption data in the form of % conversion of the zinc oxide to zinc sulfite were obtained, no attempt was made to optimize the system, or to determine process conditions for a practical fluidized zinc oxide system.

The following conclusions were drawn from the results of the experiments described above:

- Both zinc sulfite, produced from commercial pellet-size zinc oxide, and the zinc oxide regenerated from this sulfite show considerable resistance to attrition at particle sizes of -12+24 mesh and at gas velocities of 2.9 fps.
- The elutriated fines entrained in the absorber exit gas amounted to less than 0.02% of the product rate (reacted absorbent leaving absorber).
- Regeneration can be accomplished without recourse to fluidization if this appears desirable.
- Since the regenerated pellets did not agglomerate during calcination in a static system, it appears that regeneration of pellets could be accomplished in a static or rotary calciner.

IV. SCREENING OF SELECTED FLUIDIZED BASIC MATERIALS AS SO_2 ABSORBENTS

A. INTRODUCTION

The preceding discussion has dealt with the use of fluidized zinc oxide as an absorbent for SO_2. In principle, any sufficiently basic material should also be effective for SO_2 absorption, and on this basis a brief screening program was conducted involving bases other than zinc oxide. The results of this work are presented in the following sections.

B. ALKALI AND ALKALINE EARTH SULFITES

A magnesium system of interest was considered to be that involving conversion of the sulfite to the bisulfite or pyrosulfite, followed by thermal decomposition of either of these products to yield SO_2 and the sulfite:

$$MgSO_3 \cdot 3\,H_2O + SO_2 \longrightarrow Mg(HSO_3)_2 + 2\,H_2O \quad (17)$$

or

$$MgSO_3 \cdot 3\,H_2O + SO_2 \longrightarrow MgS_2O_5 + 3\,H_2O \quad (18)$$

Magnesium sulfite exists as the trihydrate, $MgSO_3 \cdot 3\,H_2O$, above 40°C, and an attempt was therefore made to convert the commercially available hexahydrate to the trihydrate before the introduction of SO_2 into the absorption bed at 50°C. It was considered that the experimental results obtained from this aspect of the study should also be of value in future work pertaining to an investigation of the disproportionation of magnesium sulfite.

The hexahydrate, which was determined to be 99.4% pure by iodometry, was screened with standard Tyler screens, and the fraction in the range 60 to 100 mesh was used exclusively. A sample of this material showed a weight loss of 41.1% when placed in an oven at 130°C for 30 minutes followed by cooling in nitrogen. Inasmuch as the theoretical weight loss for conversion to the trihydrate is 25.4%, it appeared that some loss of SO_2 might also have occurred. This was confirmed by noting that the vapor above a heated sample decolorized starch-iodide paper which had been exposed to iodine, and is of interest in connection with work reported by Ketov and Pechkovskii (Reference 3), who found that about 0.7% of the available SO_2 was liberated when a stream of nitrogen was passed over the trihydrate for 15 minutes at 300°C. In order to obtain the pure trihydrate, the sulfite can be precipitated from aqueous solution at temperatures above 40°C. However, it was decided to pursue the initial SO_2-absorption studies with the hexahydrate.

A run was conducted with 0.24 vol-% SO_2 in N_2 at 50°C with 33 ml (27.4 g) of the hexahydrate in a one-inch diameter glass tube. The space velocity of the dry gas under these conditions was 1050 hr^{-1}. The water sparger was also maintained at 50°C. Only 0.15 g SO_2 per 100 g of sulfite was absorbed before the absorption rate fell rapidly to zero. Thus, magnesium sulfite does not appear as a candidate absorbent for SO_2 under the conditions employed.

An additional run was conducted with calcium sulfite, which was determined to be 92.5% pure by iodometry. Extensive balling of the material occurred on attempted screening, and consequently the unscreened sulfite was utilized for absorption. Considerable channeling of the gas occurred during the run, even at the highest setting of the vibrator table control (see Figure 1), and no absorption of SO_2 was effected at the 50°C temperature employed.

Notwithstanding the results noted above for magnesium and calcium sulfites, it was decided to investigate alkali metal sulfites as absorbents, on the basis that these compounds are water-soluble, whereas the magnesium and calcium salts are not. It was considered that high water solubility would be effective in promoting the formation of a mono-layer of water vapor at the absorbent surface, which in turn is believed to be an important factor in effecting the absorption step. Of some concern, however, was the possibility of defluidization of the bed. This would be expected to occur if the absorption were effected under conditions such that the absorbent became deliquescent. For a water sparger temperature of 50°C, the influent gas to the absorber will contain a partial pressure of about 92 mm of water at saturation, so that deliquescence should occur for a given absorbent at all temperatures below which a saturated aqueous solution of the absorbent exhibits a vapor pressure of 92 mm.

Sodium sulfite was found to be ineffective in absorbing SO_2 at a bed temperature of 60°C. Fluidization was poor for this system at the space velocity employed (about 1140 hr^{-1}), because of the high bulk density of the solid. However, if the sulfite had been an effective absorber some absorption would have been anticipated, even under static bed conditions. It was concluded, therefore, that either absorption does not occur, or that the resulting sodium bisulfite, $NaHSO_3$ or, more likely, sodium pyrosulfite, $Na_2S_2O_5$, exhibits an appreciable decomposition pressure of SO_2 at 60°C.

Potassium sulfite was found to be deliquescent at 60°C with the water sparger at 50°C, so that the effectiveness of the dry salt could not be determined under the conditions employed. A higher bed temperature could be used to counteract deliquescence, but in view of available data relating to the Wellman-Lord process (Reference 9), in which SO_2 is stripped from a hot aqueous solution of potassium bisulfite, it was concluded that at higher bed temperatures the SO_2 decomposition pressure of potassium pyrosulfite would be appreciable.

From the results of the various experiments described above it appears that, in general, sulfites are not sufficiently basic to permit the absorption of SO_2 under fluidized bed conditions.

C. SODIUM AND CALCIUM CARBONATES

Attention was subsequently directed to the use of selected carbonates for the absorption of SO_2. Solubility data for sodium carbonate are shown in Table 6 (Reference 10). The data indicate that with the water sparger at 50°C, deliquescence would occur at or below about 55°C. Inasmuch as sodium sulfite is in general less soluble in water than the carbonate, it would be expected that the sulfite would not deliquesce if the carbonate did not.

The results obtained for an experiment in which 60 to 200 mesh sodium carbonate was used to absorb SO_2 at 60°C are shown as Run 11 in Table 7, and the corresponding gas composition and space velocity are shown in Table 8. For simplicity at this time, NO_x was not incorporated into the gas, nor was CO_2, inasmuch as the absorbent was already in the form of the carbonate. Run 4, involving zinc oxide with a somewhat similar gas composition, is also shown in the tables for comparison. Both of these runs were terminated arbitrarily, in view of the long reaction times otherwise involved. Good fluidization was observed throughout the run involving sodium carbonate, and no water condensation occurred.

TABLE 6

THE SYSTEM SODIUM CARBONATE – WATER

t (°C)	g Na_2CO_3 per 100 g of		Solid Phase	Vapor Pressure (mm Hg)
	H_2O	Sat. Soln.		
15	16.4	14.1	$Na_2CO_3 \cdot 10\ H_2O$	12.3
25	29.4	22.7	$Na_2CO_3 \cdot 10\ H_2O$	21.4
32	45.4	31.2	$Na_2CO_3 \cdot 10\ H_2O + Na_2CO_3 \cdot 7\ H_2O$	29.0
40	48.8	32.8	$Na_2CO_3 \cdot H_2O$	43.6
50	47.5	32.2	$Na_2CO_3 \cdot H_2O$	74.1
55	-	-	$Na_2CO_3 \cdot H_2O$	95.0*
60	46.3	31.6	$Na_2CO_3 \cdot H_2O$	121.5
70	45.6	31.3	$Na_2CO_3 \cdot H_2O$	192.7
80	45.2	31.1	$Na_2CO_3 \cdot H_2O$	296.2
110	44.5	30.8	Na_2CO_3	1.19 atm
130	40.9	29.0	Na_2CO_3	2.25 atm

---

*Interpolated value

TABLE 7

REACTION OF FLUIDIZED ABSORBENTS (60-200 Mesh) WITH SELECTED FLUE GAS COMPONENTS

Run No.	Absorbent	Temp (°C)	Reaction Time (hrs)	SO_2 Absorbed (g/100 g Absorbent)	SO_2 Converted to Sulfate (%)	Absorbent Converted to Sulfite (%)
2	ZnO	50	27	55.6	0.41	67.6
4*	ZnO	55	12	24.9	0.32	29.9
11*	Na_2CO_3	60	19	22.0	38.2	25.0
14	MgO	55	23-1/2	70.5	14.1	40.5

---

* Run terminated arbitrarily

TABLE 8

GASEOUS COMPOSITIONS AND SPACE VELOCITIES FOR RUNS GIVEN IN TABLE 7

(Total gas flow approximately 600 ml per minute)

Run No.	N_2	SO_2	H_2O	CO_2	O_2	Space Velocity (hr^{-1})
	Vol-%					
2	75.8	0.29	9.40	14.8	-	1122
4	72.2	0.28	10.60	14.2	2.68	1140
11	86.5	0.28	10.50	-	2.69	1137
14	71.6	0.28	11.47	14.0	2.68	1149
-*	70.9	0.28	12.18	13.9	2.70	-

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*Theoretical values, based on flue gas leaving aqueous prescrubber at 50°C.

From the results shown in Run 11, Table 7, it is evident that extensive oxidation occurred. This is probably to be attributed both to the highly basic nature of sodium carbonate and to the appreciable water solubility of both the carbonate and sulfite, inasmuch as these circumstances are favorable to both the catalyzed and uncatalyzed oxidation of sulfite at high pH (Reference 11).

Attempts to absorb SO_2 with fluidized calcium carbonate were unsuccessful. Inasmuch as sodium and calcium carbonates are both derived from strongly basic oxides, it would appear that the lack of absorption in this case may be attributable to the marked water-insolubility of both calcium carbonate and product calcium sulfite.

D. MAGNESIUM OXIDE

In Run 14 of Table 7, results are given for 60 to 200 mesh magnesium oxide. Neither the oxide nor the sulfite are appreciably soluble in water in this case, and the run could therefore be conducted at a lower temperature than that used for sodium carbonate. In order to prevent simple condensation of water in the bed (as opposed to condensation due to deliquescence) it was necessary, as in previous runs, to maintain the bed somewhat above the sparger temperature of 50°C, and the run was accordingly conducted at 55°C. It was anticipated that carbonate formation might occur, in view of the fact that magnesium oxide is a strong base, and consequently CO_2 was incorporated into the gas, as shown in Table 3. Run 2, involving zinc oxide, is included for comparison in Table 7, inasmuch as both Runs 2 and 14 were conducted to breakthrough (the point at which 10% of the SO_2 permeated the bed).

From the results shown in Table 7, it is evident that the magnesium system is of interest as a potential absorbent for SO_2. Absorption was extensive in this case (70.5 g per 100 g of MgO), and moreover the extent of oxidation was considerably less than that observed for sodium carbonate. It may be noted at this point that the weight gain associated with the bed material for Run 14 would indicate that oxide not converted to sulfite may have been converted to carbonate.

E. CONCLUSIONS

The following conclusions have been drawn from the experiments described above:

- Sulfites are unsuitable for the absorption of SO_2 under fluidized bed conditions at low temperatures, because of their limited basicity. This is reflected in the appreciable decomposition pressures of SO_2 exhibited by the desired absorption products (such as $K_2S_2O_5$) at slightly elevated temperatures.
- Weakly basic oxides are suitable absorbents. The only example here is zinc oxide.
- Strongly basic oxides are also suitable absorbents, but these compounds may be converted to the corresponding carbonates as intermediates. If this occurs, the carbonates should rather be considered as the absorbents.
- Magnesium carbonate and possibly sodium carbonate merit further investigation as dry SO_2 sorbents, particularly in view of their relatively low cost. As in the case of zinc oxide, the successful application of these materials will depend largely on the extent to which oxidation to sulfate can be avoided.

PART THREE

PROCESS IMPROVEMENT

I. INTRODUCTION

One portion of Phase IV was concerned with effecting improvements in existing aqueous processes for the removal of SO_2 from flue gas. An area of immediate interest was that involving the disproportionation of metallic sulfites, inasmuch as this type of reaction effectively decreases the amount of SO_2 which is obtainable on thermal decomposition of the sulfite. An example is provided by the Johnstone Zinc Oxide Process (Reference 7).

In the Zinc Oxide process the flue gas is scrubbed with an aqueous solution of sodium sulfite and sodium bisulfite. Zinc oxide is mixed with the effluent liquor, forming insoluble zinc sulfite, and regenerating soluble sodium sulfite which is returned to the scrubber. The zinc sulfite is separated by filtration, dried, and calcined to produce zinc oxide, which is returned to the process, and product sulfur dioxide.

Inasmuch as some oxidation occurs in the scrubber to produce sulfate which cannot be readily calcined, the process includes provisions for its removal. The effluent scrubber liquor is treated with insoluble calcium sulfite, and the mixture is passed through a clarifier. The underflow from the clarifier, which contains the calcium sulfite, is acidified with a port[illegible] of the product sulfur dioxide, thereby causing the calcium sulfite to dissolve. Calcium ion is thus made available for precipitation as calcium sulfate, which is removed by filtration and discarded. The filtrate is treated with lime to precipitate calcium sulfite, and it is then returned to the clarifier.

The following represent the important process reactions:

Scrubber:

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2\ NaHSO_3 \qquad (19)$$

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4 \qquad (20)$$

Liming Tank:

$$2\ NaHSO_3 + CaO \longrightarrow Na_2SO_3 + CaSO_3\downarrow + H_2O \tag{21}$$

Gasifier:

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2 \tag{22}$$

$$Ca(HSO_3)_2 + Na_2SO_4 \longrightarrow 2\ NaHSO_3 + CaSO_4\downarrow \tag{23}$$

Mixer:

$$2\ NaHSO_3 + ZnO + 1\text{-}1/2\ H_2O \longrightarrow Na_2SO_3 + ZnSO_3 \cdot 2\text{-}1/2\ H_2O\downarrow \tag{16}$$

Calciner:

$$ZnSO_3 \cdot 2\text{-}1/2\ H_2O \xrightarrow{\Delta} ZnO + SO_2\uparrow + 2\text{-}1/2\ H_2O\uparrow \tag{24}$$

$$4\ ZnSO_3 \cdot 2\text{-}1/2\ H_2O \xrightarrow{\Delta} 3\ ZnSO_4 + ZnS + 10\ H_2O\uparrow \tag{25}$$

Reaction 25, which represents the disproportionation, occurs only to the extent of about 2 to 3 percent (Reference 12). However, both zinc sulfate and sulfide are ineffective in reabsorbing SO_2, and consequently these compounds slowly build up during processing unless provision is made for their removal. In the case of the sulfites of the alkali and alkaline earth metals (such as magnesium), the disproportionation reaction is much more extensive (Reference 13), and represents a serious deterrent to the recovery of SO_2 by thermal means.

As a first undertaking in Phase IV, attention was directed to the problem of effecting Reaction 1 and Reaction 24 to the exclusion of Reaction 25. Work on the zinc system was followed by a preliminary study involving magnesium.

II. DISPROPORTIONATION OF ZINC SULFITE

A. INTRODUCTION

The disproportionation of zinc sulfite has been investigated by several workers, including Johnstone and Singh (Reference 12), Okabe, et al. (Reference 14), Cola and Tarantino (Reference 15), Pechkovskii and Ketov (Reference 3), Pannetier, et al. (Reference 16), and Ingraham and Kellogg (Reference 17). The reaction is thermodynamically favored in the temperature range 25° to 800°C (Reference 18), but the kinetics are such that the simple decomposition of the sulfite (Reaction 24) is highly predominating. The following comments summarize the more important findings of the studies considered above:

- The precursor to disproportionation is the formation of a basic sulfite having the formula $ZnSO_3 \cdot ZnO$.
- The oxidation of the precursor can be effected with either atmospheric oxygen or with SO_2, forming a basic sulfate.
- No disproportionation occurs at or below 300°C, and the rate of disproportionation decreases with increasing temperature above 350°C.
- The addition of transition metal oxides increases the rate of disproportionation at all temperatures at which disproportionation occurs.
- The final composition of the basic sulfate which appears as one disproportionation product is probably $ZnO \cdot 2\ ZnSO_4$. A compound exhibiting the composition $ZnO \cdot ZnSO_4$ may form as a relatively unstable intermediate.

From the above discussion it is apparent that Reaction 25 represents an over-simplification of the disproportionation process. The fact that the reaction occurs most readily in the temperature range of 300° to 350°C implies that the present thermal decomposition studies should be limited to temperatures lying outside this range. Initial work on the program was carried out at relatively high temperatures and for short reaction times. Later work was devoted to low temperatures for extended reaction times.

B. RESULTS OF EXPERIMENTS CONDUCTED IN A MUFFLE FURNACE

Johnstone and Singh (Reference 12) investigated the thermal decomposition of zinc sulfite in an electric muffle furnace at 375°, 425°, and 475°C for time periods ranging from 15 minutes to 3 hours. Under these conditions the formation of sulfate varied from about 2 to 5 percent. It was considered of interest to investigate the use of higher temperatures and shorter reaction times than those employed by Johnstone and Singh, for the purpose of determining whether or not the rate of sulfate formation is slow relative to the rate of decomposition of the sulfite at the relatively high temperatures of interest.

A series of experiments (delineated in Table 9) was conducted with $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ which, by iodometry, was found to be 92.2% pure. From the weight loss observed on subsequent calcination of this material it was concluded that the principal impurity was probably surface water. In carrying out the experiments the sample, contained in a crucible, was placed on a preheated petri dish in a muffle furnace and was immediately covered with a preheated cover and heated for a specified time, after which the petri dish, crucible, and cover were removed and cooled in a vessel through which a stream of nitrogen was passed. Decomposition runs at about 545°C were conducted for 5, 15, and 45 minutes, the decomposition being complete (i.e., no sulfite present by iodometry) even after 5 minutes. That appreciable sulfide was not present in any of the residues (compare Reaction 25) was also shown by iodometry, inasmuch as acidified samples of the residues required no iodine, and no detectable sulfur formed:

$$H_2S + I_2 \longrightarrow 2\ HI + S\downarrow \qquad (26)$$

TABLE 9

THERMAL DECOMPOSITION OF $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ IN A MUFFLE FURNACE AT 545 ± 3°C

Reaction Time (min)	Conversion of Available SO_2 to $SO_4^=$ (%)	Available SO_2 Released (%)	Remarks
15	3.92	96.1	Covered crucible
45	4.51	95.5	" "
5	4.94	95.1	Uncovered crucible
45	4.84	95.2	" "

It was noted, however, that the acidified solutions exhibited a very faint odor of H_2S, and that a very faint positive test was always obtained with moistened lead acetate paper in the vapor phase above the solutions:

$$H_2S + Pb(CH_3COO)_2 \longrightarrow \underset{\text{black}}{PbS\downarrow} + 2\ CH_3COOH \qquad (27)$$

The above series of experiments was repeated, except that the preheated crucible cover was left off during the runs, but was used to cover the crucible at the time of removal from the muffle and during subsequent cooling. It was considered that when the sulfite was heated in an open vessel the atmosphere present at the solid surface would be somewhat different from that present in the closed vessel. In the open vessel the decomposing basic sulfite (Reaction 4) would be exposed to SO_2, H_2O, and O_2, the latter being present as part of the air originally contained in the muffle at the time of introduction of the sample. These compounds would be expected to compete with the thermal decomposition of the basic sulfite, giving rise to sulfate formation (Reference 3):

$$ZnSO_3 \cdot ZnO + 1/2\ O_2 \longrightarrow ZnSO_4 \cdot ZnO \qquad (28)$$

$$2\ (ZnSO_3 \cdot ZnO) + SO_2 \longrightarrow 2\ ZnSO_4 \cdot ZnO + 1/2\ S_2 \qquad (29)$$

Although it has been reported (Reference 3) that the sulfur liberated in Reaction 29 reacts further to yield zinc sulfide, the temperature of the muffle in the present experiments ($\sim 545^{\circ}C$) was above that of the boiling point of sulfur ($444^{\circ}C$), so that it might be expected that the reaction involving sulfur would not be extensive:

$$4\ ZnO + 3\ S_2 \longrightarrow 4\ ZnS + 2\ SO_2\uparrow \qquad (30)$$

For the series of experiments in which the crucible was covered during the calcination, the basic sulfite should have been exposed to SO_2, but not to O_2 or H_2O. The reason for this is that the air and water would have been displaced many times over with SO_2 before the basic sulfite had formed appreciably. It was calculated that in the early part of the decomposition, corresponding largely to a loss of water of crystallization, some 54 replacements of the atmosphere contained within the crucible would occur (thus completely displacing the air originally present), and that the subsequent liberation of SO_2 to yield the oxide would result in 22 additional atmosphere replacements. It was considered that the results obtained under these conditions, insofar as the formation of sulfate is concerned, might differ appreciably from those observed when the crucible was not covered, and that in particular a reaction of the basic sulfite with the dry SO_2 present when the crucible was covered (Reaction 29) might not readily occur.

The residues obtained from the calcination experiments in open crucibles were in general quite similar to those obtained earlier. The calcination was complete within 5 minutes as before, and only very faint tests were observed for the presence of sulfide.

During the course of the experiments in open crucibles described above, it was noted that the percentage weight loss of the sulfite on calcination was the same for both 5 min and 45 min heating periods. These results are in contrast to those reported by Johnstone and Singh (Reference 13), who indicated that infiltration of air into the muffle, and the subsequent reabsorption of SO_3 by the zinc oxide, was probably responsible for the observed oxidation to sulfate; i.e.,

$$ZnO + SO_2 + 1/2\ O_2 \longrightarrow ZnSO_4 \qquad (31)$$

In order to obtain additional information on this point an experiment was conducted in which a covered sample of zinc sulfite was calcined in the presence of an uncovered sample of zinc oxide (Kadox-15, 99.7% pure). If it is assumed that the decomposition of the sulfite resulted in the displacement of air only from the furnace, the resulting atmosphere within the furnace should have consisted of 9.1% O_2, 15.5% SO_2, 38.9% H_2O, and 36.5% N_2. It was found that Reaction 31 did not occur when the zinc oxide sample was maintained for a one-hour heating period in this atmosphere, and that in fact a small loss in weight of the oxide occurred as the result of a loss of surface moisture.

Samples of the various decomposition residues from the experiments discussed above were analyzed for contained sulfate, and in all cases an appreciable quantity was found. The data, which are shown in Table 9, indicate that sulfate formation occurs primarily during the actual decomposition, and that the subsequent heating of the decomposition residue in the presence of SO_2 does not lead to an appreciable increase in sulfate. The somewhat lower sulfate values obtained for the decomposition in closed crucibles may indicate a decreased reaction rate in the absence of water vapor, since under the conditions employed the water of hydration of the sulfite would have been displaced from the crucible by the SO_2 subsequently liberated. The absence of sulfide in the residues is attributed to the high calcination temperatures used, in that volatilization of intermediate free sulfur (boiling point 444°C) would be expected (Reference 3):

$$2\ ZnSO_3 \cdot 2\text{-}1/2\ H_2O \longrightarrow ZnSO_3 \cdot ZnO + SO_2\uparrow + 5\ H_2O\uparrow \qquad (3)$$

$$2\ (ZnSO_3 \cdot ZnO) + SO_2 \longrightarrow 2\ (ZnSO_4 \cdot ZnO) + 1/2\ S_2\uparrow \qquad (29)$$

$$4\ ZnO + 3\ S_2 \not\longrightarrow 4\ ZnS + 2\ SO_2\uparrow \qquad (30)$$

Inasmuch as sulfate formation is known to occur through reaction of the basic sulfite, $ZnSO_3 \cdot ZnO$, with SO_2 (Reaction 29), it would appear that the rapid removal from the reaction zone of the SO_2 liberated in Reaction 3 should tend to inhibit Reaction 29. The rapid removal of SO_2 should be most effective at relatively low temperatures, where Reaction 29 is slow. Accordingly, experiments were subsequently conducted in which zinc sulfite was decomposed at 275 ± 3°C but for an extended time. This temperature was chosen as lying between the minimum temperature required for the complete decomposition of the sulfite at a total pressure of one atmosphere (about 260°C, References 19 and 20), and the temperature at which disproportionation is purported to begin (300° to 350°C, Reference 3). At 250°C, for example, decomposition (Reaction 24) was found by Johnstone to occur to the extent of only about 62% in a muffle furnace before equilibrium was reached (Reference 21), whereas at 350°C disproportionation (Reaction 25) occurs to the extent of about 4% (Reference 3).

The results of experiments conducted in the muffle furnace at 275°C are shown in Table 10. The decomposition was complete only after 6 hours, with the slowness of the reaction resulting in a much greater difference in the use of covered versus uncovered crucibles than that which was observed in the earlier experiments at 545°C. In this series of experiments, the slower decomposition rate in covered crucibles indicates that SO_2 (which should be the main constituent of the ultimate atmosphere within the crucible) has an inhibiting effect on the decomposition. Also, the relatively low sulfate content of the residue under these conditions shows that SO_2 does not cause appreciable disproportionation at the temperature employed. It was observed, in fact, that hydrochloric acid solutions of the decomposition residues exhibited no odor of H_2S, gave negative tests with lead acetate paper, and gave no precipitate of copper sulfide with copper ion. The residues were completely soluble in the acid, and consequently contained no free sulfur. These results indicate the complete absence of disproportionation, so that the observed sulfate must in all cases have resulted from oxidation by atmospheric oxygen. This explanation is in keeping with the greater observed oxidation for uncovered crucibles in that the contents of these crucibles were exposed to the air present within the furnace, and implies that in the case of covered crucibles the oxidation largely occurred during the early part of the decomposition, before the displacement of air was complete. In this connection it may be noted from the table that in general little or no oxidation occurred during the final stages of the decomposition.

It was considered that the experiments conducted in the muffle furnace were of value in providing general information relating to the decomposition of the sulfite as a function of temperature, and to some extent as a function of atmospheric composition. However, the employment of a much more closely controlled atmosphere is possible through the use of a tube furnace, and accordingly attention was subsequently directed to the use of this type of furnace.

TABLE 10

THERMAL DECOMPOSITION OF $ZnSO_3 \cdot 2\ 1/2H_2O$ IN A MUFFLE FURNACE AT 275 ± 3°C.

Reaction Time (hrs)	SO_2 Released (%)	SO_2 Converted to Sulfate* (%)	SO_2 Total* (%)	Remarks
1 1/2	62.7	1.41	64.1	Covered crucible
2	68.0	1.36	69.4	" "
1	70.4	3.44	73.8	Uncovered crucible
2	87.8	3.74	91.5	" "
3	93.5	3.68	97.2	" "
6	96.6	3.36	100.0	" "

* **Zinc sulfide was not observed as a product; therefore, observed sulfate formation resulted from oxidation of sulfite by atmospheric oxygen rather than from disproportionation reaction.**

C. RESULTS OF EXPERIMENTS CONDUCTED IN A TUBE FURNACE

The results of a fairly extensive series of experiments which were conducted at 275 ± 3°C in a 12-inch tube furnace are shown in Table 11. The experimental apparatus consisted of the gas metering system shown in Figure 2, a water sparger which was used in some of the runs, the tube furnace, a bubbler (filled with either standard iodine or dilute caustic solution) for trapping acid gases, and a wet test meter. A 1 in. dia x 18 in. long glass tube was employed within the furnace, with the sample placed in a glass boat at the center of the tube. The temperature immediately above the sample was monitored through the use of a chromel-alumel thermocouple placed in a glass thermal well.

In operation, a gas of predetermined composition was caused to flow through the furnace at 3 liters/hr and an approximately 0.5 g sample of the sulfite was subsequently introduced into the furnace through the thermal well port. At the completion of the run the sample boat was moved upstream to a cold portion of the tube, and allowed to cool in a current of the gas which had been used during the decomposition of the sulfite. The decomposition residue was then analyzed by iodometry for undecomposed sulfite, and by barium sulfate precipitation (turbidimetric method) for contained sulfate. Excess iodine in the bubbler was back titrated with standard thiosulfate to determine the amount of SO_2 released. However, in those runs (see Table 11) in which oxygen was present as a component of the carrier gas, the iodine bubbler was not used because of a possible interfering oxidation of HI by oxygen, and in these instances the SO_2 release was determined by difference, as noted in the table. Whenever SO_2 was deliberately introduced as a gaseous component, the accuracy of the determination of the SO_2 released by the sample was severely limited; in these cases the SO_2 released was also determined by difference.

The most significant result of the experiments conducted in the tube furnace is that indicating the marked effect of even small amounts of water vapor on the rate of decomposition of the sulfite. From the data in

TABLE 11

THERMAL DECOMPOSITION OF $ZnSO_3 \cdot 2\ 1/2\ H_2O$ IN A TUBE FURNACE AT 275 ± 3°C.

Run No.	Reaction Time (hrs)	SO_2 Released[1] (%)	SO_2 Retained (%)	SO_2 Converted to Sulfate[2] (%)	SO_2 Total[3] (%)	Gas Composition[4]
1	1	48.0	49.2	0.76	98.0	0.03 H_2O in N_2
2	6	61.6	36.4	0.91	98.9	"
3	1	49.2	45.5	1.16	95.9	1.01 H_2O in N_2
4	2	80.4	15.9	1.68	98.0	"
5	1	77.8	15.8	1.30	94.9	2.27 H_2O in N_2
6	2	92.1	5.1	1.35	98.6	"
7	1	(54.0)	41.1	2.33	97.4[5]	21 O_2 + 0.36 H_2O in N_2
8	2	(74.4)	20.5	2.49	"	"
9	3	(79.7)	15.4	2.25	"	"
10	1	(85.3)	8.6	3.45	"	21 O_2 + 2.27 H_2O in N_2
11	3	(93.3)	0.7	3.39	"	"
12	1	(41.4)	55.9	0.13	"	5 SO_2 in N_2
13	2	(41.2)	56.0	-0.17	"	"
14	3	(41.1)	56.6	-0.26	"	"
15	1	(57.3)	39.0	1.07	"	5 SO_2 + 2.27 H_2O in N_2
16	3	(78.5)	17.4	1.48	"	"

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[1] Values in parentheses were obtained by difference from the total SO_2.

[2] The zinc sulfite used in these studies contained 4.5% sulfate, and a negative value in this column indicates that less sulfate was observed in the product than in the starting material.

[3] Zinc sulfide was not observed as a product in any of the runs.

[4] All values are given in volume per cent. The gas flow rate was always 3.0 l/hr. The water content of the various gas mixtures was determined by passing the gas through Desicchlora (anhydrous barium perchlorate).

[5] This value was determined as the average of the values obtained in Runs 1 to 6.

Table 11 it may be noted that when essentially water-free nitrogen was used as the carrier gas, approximately one-half of the SO_2 was released during one hour (Run 1), and that, even after 6 hours, only 61.6% of the available SO_2 had been released (Run 2). With small, but increasing, amounts of water in the gas phase, the decomposition rate progressively increased (Runs 4 and 6), and was essentially complete at the end of 2 hours (Run 6). That added water was less effective during the first hour (compare Run 1 with Run 3) can be attributed to the fact that appreciable water was already available during the initial stages of the decomposition as a result of the release of the water of crystallization of the sulfite.

As in the case of the experiments carried out in the muffle furnace, the residues from the tube furnace contained no sulfide or free sulfur. Thus Reaction 29 does not occur at 275°C, and the formation of sulfate shown in Table 11 is presumed to be due to the presence of oxygen. It will be noted, in comparing Runs 1 and 2, that the small amount of oxidation would be favored at this time by the release of water of crystallization (compare Runs 1-2 with Runs 3-4 and 5-6, and Runs 7-9 with Runs 10-11, where water is seen to promote oxidation), and presumably is effected by occluded air on the surface of the solid, and/or by air admitted to the tube during the introduction of the sample. That oxidation is not due to disproportionation is further indicated by a comparison of the results obtained in Runs 12-14 with those obtained in Runs 1-2. The data not only indicate that Reaction 29 does not occur, but further show that the presence of dry SO_2 is effective in inhibiting oxidation by oxygen. The SO_2 presumably complexes with any water present, and the oxidation of sulfite does not proceed in the dry state:

$$ZnSO_3 \cdot 2\text{-}1/2\ H_2O + 1/2\ O_2 \not\longrightarrow ZnSO_4 + 2\text{-}1/2\ H_2O \qquad (32)$$

$$ZnSO_3 \cdot ZnO + 1/2\ O_2 \not\longrightarrow ZnSO_4 \cdot ZnO \qquad (28)$$

Johnstone noted that wet zinc sulfite cake became hot when it stood in contact with air in the laboratory, and that considerable oxidation took place (Reference 22). On the other hand, in Aerojet laboratories the routine handling of dry zinc sulfite over several months did not result in an increase in the amount of sulfate (about 4.5%) present at the time of purchase. The effect of water in promoting the oxidation by oxygen can be further seen by comparing Runs 7-9 with Runs 10-11.

From a comparison of Runs 1-2 with Runs 12-14 it appears that the presence of SO_2 in the gas phase tends to inhibit the decomposition reaction, and this effect was noted earlier in connection with experiments conducted in the muffle furnace. This indicates that Reaction 1 is reversible. However, the presence of water in the gas phase tends to counteract this effect, as shown by a comparison of Runs 15-16 with Runs 12-14.

In both Tables 10 and 11 the data relating to the conversion of sulfite to sulfate indicate in some instances that a slight decrease in sulfate content occurs on prolonged heating. However, this is considered not to be the case, inasmuch as it was found that the heating of $ZnSO_4 \cdot 7\ H_2O$ for 6 hours at 275 ± 3°C in the tube furnace in a current of nitrogen did not result in decomposition. From the weight of the residue it was calculated that all of the water had been lost, but analyses of the caustic solution through which the off-gas had been sparged indicated that neither SO_2 nor SO_3 had been evolved. It appears, therefore, that the lack of agreement in the data pertaining to sulfate must be attributed to experimental error. It may be stated that the experimental values of SO_2 retained and SO_2 released shown in Tables 10 and 11 are probably accurate to about 1%, but that the values for SO_2 converted to sulfate are accurate to no more than 5%. This arises from the use of the turbidimetric method used for sulfate, which is somewhat less accurate than the corresponding gravimetric method (1%). However, in view of the large number of sulfate analyses which had to be conducted both on this and other phases of the program, it was considered that the more tedious gravimetric method was impractical.

In summary, it appears that the decomposition of zinc sulfite can be carried essentially to completion in about 2 hours (Run 6) at a temperature (275°C) which is sufficiently low so that the disproportionation of the sulfite does not occur. This is accomplished by introducing a small amount of water into the gas phase as an aid to the removal of the combined SO_2. The water of crystallization also serves the function of aiding in the removal of the SO_2. Disproportionation (sulfate and sulfide formation) does not occur at the temperature employed, but oxidation (sulfate formation) will occur whenever oxygen (air) is present. It follows that in the practical case the calcination of the sulfite should be effected in the absence of air.

Inasmuch as a small amount of water is effective in aiding the liberation of SO_2 from the sulfite, it was obviously of interest to investigate the use of steam for promoting the decomposition at a somewhat lower temperature. The use of a lower temperature is desirable both from the standpoint of reducing fuel costs for effecting the decomposition, and of decreasing the rate (and therefore extent) of oxidation of the sulfite.

The effect of steam on the decomposition reaction is shown in Table 12. Some of the data (Runs 1 to 6) were also given in Table 11, but are included for comparison. Run 20 was conducted in order to obtain additional data relating to the manner in which the decomposition occurs. According to Pennetier (Reference 16), the first step involves partial dehydration at 90° to 100°C as follows:

$$ZnSO_3 \cdot a\text{-}1/2\ H_2O \xrightarrow{\Delta} ZnSO_3 \cdot 1/2\ H_2O + 2\ H_2O\uparrow \qquad (33)$$

In view of the general tendency toward increased SO_2 release through the incorporation of water vapor in the gas phase at 275°C (compare Runs 1 to 6), and because precisely one-half of the available SO_2 in the sulfite was released during the first hour when very little water was incorporated in the gas phase (Runs 1 and 3), it was considered that the further loss of water from the product of Reaction 33 might be accompanied by a corresponding loss of SO_2; that is,

$$2\ ZnSO_3 \cdot 1/2\ H_2O \xrightarrow{>100^\circ C} ZnSO_3 \cdot ZnO + SO_2 \cdot H_2O\uparrow \qquad (34)$$

TABLE 12

EFFECT OF WATER VAPOR ON THE THERMAL DECOMPOSITION OF $ZnSO_3 \cdot 2\,1/2\,H_2O$ IN A TUBE FURNACE

Run No.	Temp (± 3°C)	Reaction Time (hrs)	SO_2 Released (%)	SO_2 Retained (%)	SO_2 Converted to Sulfate (%)	SO_2 Total* (%)	Gas Flow Rate (1/hr)	Gas Composition (vol-% H_2O in N_2)
19	225	2	17.2	78.6	0.24	96.0	3.0	0.03
20	275	1/4	29.6	67.3	0.00	96.9	"	"
1	"	1	48.0	49.2	0.76	98.0	"	"
2	"	6	61.6	36.4	0.91	98.9	"	"
3	"	1	49.2	45.5	1.16	95.9	"	1.01
4	"	2	80.4	15.9	1.68	98.0	"	"
5	"	1	77.8	15.8	1.30	94.9	"	2.27
6	"	2	92.1	5.1	1.35	98.6	"	"
17	225	2	36.9	60.0	0.04	96.9	4.4	91.0
18	275	1/2	81.5	14.1	0.92	96.5	3.5	93.5

* Zinc sulfide was not observed as a product in any of the runs.

Although Reaction 34 may occur to some extent, the results of Run 20 show that the loss of water from the hemihydrate is not necessarily accompanied by the loss of SO_2. In Run 20 it was observed that all of the available water was lost during the 15 minute duration of the run, but only 29.6% of the available SO_2 was released.

Run 19 shows the marked decrease in the rate of the decomposition reaction when the temperature is decreased from 275°C to 225°C (compare Run 19 with Runs 20, 1, and 2). The use of steam as the carrier gas is effective at this temperature, as shown in Run 17. However, the complete decomposition of the sulfite at 225° would require several hours, even in the presence of steam.

In Run 18 it will be noted that the decomposition can be carried nearly to completion during one-half hour at 275° when steam is employed as the carrier gas (compare Run 18 with Runs 20 and 1). The small amount of sulfate which was observed to form at this temperature is attributed to the presence of air, as discussed above. Although the data indicate a release of 81.5% of the available SO_2, this result, as well as the results pertaining to SO_2 release in all of the other runs, is undoubtedly somewhat low. It was noted during the latter stages of the work that a small amount of SO_2 was escaping through each of two pyrex ball joints located downstream of the furnace, but upstream of the bubbler used to entrain the SO_2. This observation is considered to explain the deviation of the total SO_2 observed from 100 percent, and indicates that the data relating to SO_2 release are probably better derived from the data for the SO_2 retained. Thus, in the case of Run 18, the SO_2 released is considered to be 100-14.1-0.9 or 85.0%.

The results of Run 18 indicate that it should be possible to carry out the decomposition of zinc sulfite in the neighborhood of 275°C in the practical case without concurrent disproportionation. Since the latter reaction occurs only at temperatures exceeding 300°C (Reference 3), the decomposition temperature could be increased somewhat (say to 290°C) if it were desired to complete the reaction in a shorter time. The reaction would perhaps best be accomplished in a fluidized bed regenerator, so designed that the steam liberated in Reaction 24 would be available to assist in the final stages of the decomposition. The formation of sulfate would be avoided by effecting the decomposition in the absence of air, and the regenerator would preferably be maintained at a slight positive pressure to prevent air leakage.

No further work was conducted relating to the disproportionation of the zinc sulfite, since it was considered that the experimental conditions required for decomposing the sulfite without attendant disproportionation have now been defined. Accordingly, attention was subsequently directed to the effect of steam on the disproportionation of magnesium sulfite.

III. DISPROPORTIONATION OF MAGNESIUM SULFITE

Magnesium oxide has been found to be effective in removing SO_2 from gas streams in fluidized bed systems (see Table 7), and it also appears that it can be substituted for ZnO in the Johnstone process (see Table 4 and the accompanying discussion). It was of interest, therefore, to optimize the regeneration of MgO from $MgSO_3 \cdot 6\ H_2O$, since extensive disproportionation occurs during the thermal decomposition of the sulfite. A brief laboratory investigation was conducted to determine if steam would lower the effective decomposition temperature and/or lower the amount of disproportionation of $MgSO_3 \cdot 6\ H_2O$. The 12-inch tube furnace that was utilized in the studies relating to the decomposition of zinc sulfite was also used in this investigation. An analysis of the magnesium sulfite indicated 90.4 wt-% $MgSO_3 \cdot 6\ H_2O$ and 5.7 wt-% $MgSO_4$.

Elemental sulfur was produced in small amounts during the decomposition of the sulfite and condensed on the side of the tube downstream of the furnace. The sulfur was dissolved in CS_2 and its weight determined after evaporation of the solvent. The residue in the boat was weighed and divided into two parts for analysis. The first part was analyzed for unreacted $SO_3^=$ by adding a known quantity of 0.1 N iodine, then enough 0.1 N HCl was added to dissolve the solid phase, and finally the solution was back titrated with 0.1 N sodium thiosulfate. If any thiosulfate was found in the second analysis, described below, a correction was made for it, since it also consumes iodine.

The second part of the solid residue was analyzed for sulfate and thiosulfate by the following procedure. Ten ml of concentrated HCl was added to the sample, which was evaporated to dryness at 130°C. Twenty-five ml of water was then added, and the solution was heated to boiling. The hot solution was filtered, and the residue washed with water. The filtrate was cooled to room temperature, and sulfate determined turbidimetrically. The residue was dried at 110°C, cooled, and reweighed as sulfur, which is a measure of the thiosulfate in the sample.

The following equations represent the reactions involved in the second part of the analysis:

$$SO_3^{=} + 2\ HCl \longrightarrow SO_2 + H_2O + 2\ Cl^{-} \qquad (35)$$

$$S_2O_3^{=} + 2\ HCl \longrightarrow SO_2 + S\downarrow + H_2O + 2\ Cl^{-} \qquad (36)$$

Several samples of pure MgS_2O_3 were analyzed in the above manner and sulfur representing 96% of that shown in Reaction 36 was found. Since the temperature of the furnace was above the boiling point of sulfur in all runs, no appreciable quantity of free sulfur could have been left in the solid residue.

The results of three of the best runs are given in Table 13. Only those runs with a sulfur balance of 95-105% are reported. The results of the Russian investigators Ketov and Pechkovski (Reference 3) are reported for comparison. At 450°C with a nitrogen gas purge (Run 2), the total conversion of S in the sulfite was 34.1% compared with 38.3% reported by the Russian investigators. The amount of sulfate formed (14.7%) also compared well with theirs (12.9%). The amounts of sulfur and thiosulfate formed, however, were appreciably less than those found by the Russian investigators. A similar analysis can be made of the runs made at 550°C.

Run No. 9 was made at 450°C, with the purge gas consisting of 85% steam and 15% nitrogen. This run indicates that the total conversion of sulfur in the sulfite increased to 57.9% (compare with Run 2 using nitrogen). It appears,

TABLE 13

EFFECT OF TEMPERATURE ON THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE IN A CURRENT OF NITROGEN OR STEAM AND NITROGEN

Run No.	Temp. ± 5°C	Reaction Time hr	Purge Gas	% Conversion of S in Sulfite to				Total Reacted %	$SO_3^=$ Not Reacted %	S Balance %
				SO_2	MgS_2O_3	S	$MgSO_4$			
2	450	1/3	N_2	17.1	0.8	1.5	14.7	34.1	66.4	100.5
*	450	1/4	N_2	16.3	5.3	3.8	12.9	38.3	-	-
9	450	1/3	85% steam 15% N_2	41.4	0.0	2.4	14.1	57.9	41.4	99.3
4	550	1/3	N_2	81.5	0.0	5.6	15.1	102.2	1.8	104.0
*	550	1/4	N_2	68.5	0.0	8.4	17.5	94.4	-	-

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*Reference 3.

however, that the quantity of sulfate formed was not lowered, due to addition of steam to the purge gas. It should be noted that the quantity of sulfate formed did not change significantly at the higher decomposition temperature.

This brief investigation is not conclusive, but it appears that:

- Steam will assist decomposition of magnesium sulfite and should reduce the decomposition temperature.
- Steam apparently will not lower the percent of magnesium sulfate formed during disproportionation.

A more thorough study is needed to verify these assumptions.

IV. THERMAL DECOMPOSITION OF ZINC SULFATE

From the data given in Tables 1 and 2, it appears that the use of ferrous ion in a prescrubber can, under optimum conditions, essentially eliminate the formation of sulfate in a fluidized zinc oxide absorber. It may be presumed, however, that in practice, traces of sulfate probably will form, and it was therefore considered of interest to briefly investigate the thermal decomposition of zinc sulfate. In particular, it was considered that the use of steam might be effective in lowering the calcination temperature of the sulfate, inasmuch as steam has been observed to promote the decomposition of both zinc and magnesium sulfites to a marked extent.

Considerable discrepancy exists in the literature relative to the temperature required to decompose zinc sulfate to the oxide. According to Margulis and Remizov (Reference 24), the decomposition occurs in two stages, as follows:

$$3\ ZnSO_4 \xrightarrow{>610^\circ C} ZnO\cdot 2\ ZnSO_4 + SO_3\uparrow \qquad (37)$$

$$ZnO\cdot 2\ ZnSO_4 \xrightarrow{>740^\circ C} 3\ ZnO + 2\ SO_3\uparrow \qquad (38)$$

Pannetier (Reference 16) noted that the basic sulfate that formed from the thermal decomposition of zinc sulfite in the presence of oxygen, and which he formulated as $ZnO\cdot 2\ ZnSO_4$ (compare Reaction 38), decomposed at 854°C.

On the other hand, Pechkovskii and Ketov (Reference 3), reported the formation of a basic sulfate of unknown composition from the disproportionation of the sulfite, and observed that the sulfate decomposed in the temperature range 993° to 1027°C.

The experimental results from this study are shown in Table 14. The apparatus used was that described earlier for the decomposition of the corresponding sulfite in a tube furnace at 275°C, except that the gas entering the furnace was preheated through the use of heating tape in those experiments in which steam was used in order to prevent water condensation, and the exiting gas was similarly heated to prevent the condensation of sulfuric acid. The steam was supplied to the furnace by passing a small amount of nitrogen through a water sparger maintained at approximately 100°C. The effluent gas was sparged through a caustic bubbler, which was subsequently neutralized with acid and analyzed for SO_2 content. The values for SO_3 released shown in the table were derived by difference from the SO_3 retained by the partially decomposed residue.

The decomposition of the sulfate would be expected to yield SO_3 as a primary decomposition product following the loss of water:

$$ZnSO_4 \longrightarrow ZnO + SO_3\uparrow \qquad (39)$$

However, at higher temperatures the SO_3 dissociates:

$$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2 \qquad (40)$$

At 790°C, for example, the equilibrium constant for Reaction 40 is unity. The relatively low values for the dissociation of SO_3 shown in the table are therefore attributed to the limited SO_3 residence time at the furnace temperature.

Runs 1 to 3 in Table 14 are reported merely for completeness, inasmuch as only dehydration occurred at the relatively low temperatures employed. The direct introduction of the heptahydrate into the furnace at

TABLE 14

EFFECT OF WATER VAPOR ON THE THERMAL DECOMPOSITION OF ZINC SULFATE IN A TUBE FURNACE

Run No.	Temp (± 3°C)	Reaction Time (hrs)	H_2O Released[a] (%)	SO_3 Released (%)	Dissociation of SO_3 Released[b] (%)	Gas Flow Rate (l/hr)	Gas Composition (vol-% H_2O in N_2)
1	275	6	100	0	—	3.0	0.03
2	500	2	100	0	—	4.5	93.8
3	650	2	100	0	—	3.0	0.03
4	750	3	—	21.0	trace	3.0	0.03
5	750	3	—	35.4	trace	4.6	92.7
6	800	1	—	37.3	trace	4.4	93.2
7	850	1	—	48.7	11.52	3.0	0.03
8	850	1	—	56.0	8.51	3.7	94.3

[a] $ZnSO_4 \cdot 7H_2O$ was used in runs 1 to 3; the anhydrous salt was used in the remaining runs.

[b] $SO_3 \rightleftharpoons SO_2 + 1/2\,O_2$

temperatures exceeding 650°C was attended by considerable spattering of the solid because of the rapidity of the dehydration. Runs 4 to 8 were therefore conducted with sulfate which had been dehydrated at lower temperatures in the manner shown for Runs 1 to 3.

A comparison of Runs 4 and 5 indicates that the presence of water is beneficial at 750°C in promoting the decomposition of the sulfate. However, the rate of decomposition is very slow at this temperature. By raising the temperature to 800°C, the time can be reduced by a factor of three (Run 6), but the decomposition rate is still slow. At 850°C (Runs 7 and 8), the effect of water is less pronounced, presumably because any molecular complex involving water and SO_3 would be largely dissociated at the high temperature involved. To the extent that such complexing does exist, the dissociation of the SO_3 is depressed, as can be seen from the table.

From the data in Table 14 it is concluded that the presence of water will not materially promote the decomposition of zinc sulfate at the high temperatures required for complete decomposition. From the time-temperature data, it would be expected that a temperature in the neighborhood of 1000°C would be required for complete decomposition in a relatively short time (say, 15 to 30 minutes). This temperature is essentially that observed by Pechkovskii and Ketov, as noted in the previous discussion. If equilibrium is established at 1000°C, all of the liberated sulfur will be in the form of SO_2, rather than SO_3.

The calcination of zinc sulfate is considered further in the following section.

PART FOUR

A ZINC OXIDE FLUIDIZED BED SYSTEM FOR THE ABSORPTION AND REGENERATION OF SO_2

From the experimental results discussed in the preceding sections, it is now possible to formulate a tentative system for the removal and recovery of SO_2 from a gas stream, such as the flue gas from a power station, through the use of fluidized zinc oxide as the absorber. Such a system is shown in Figure 4. The following chemical reactions are involved:

Absorber:

$$ZnO + SO_2 + 2\text{-}1/2\ H_2O \longrightarrow ZnSO_3 \cdot 2\text{-}1/2\ H_2O \qquad (1)$$

$$ZnO + SO_2 + H_2O + 1/2\ O_2 \longrightarrow ZnSO_4 \cdot H_2O \qquad (41)$$

Regenerator (527°F):

$$ZnSO_3 \cdot 2\text{-}1/2\ H_2O \xrightarrow{\text{steam}} ZnO + SO_2\uparrow + 2\text{-}1/2\ H_2O\uparrow \qquad (24)$$

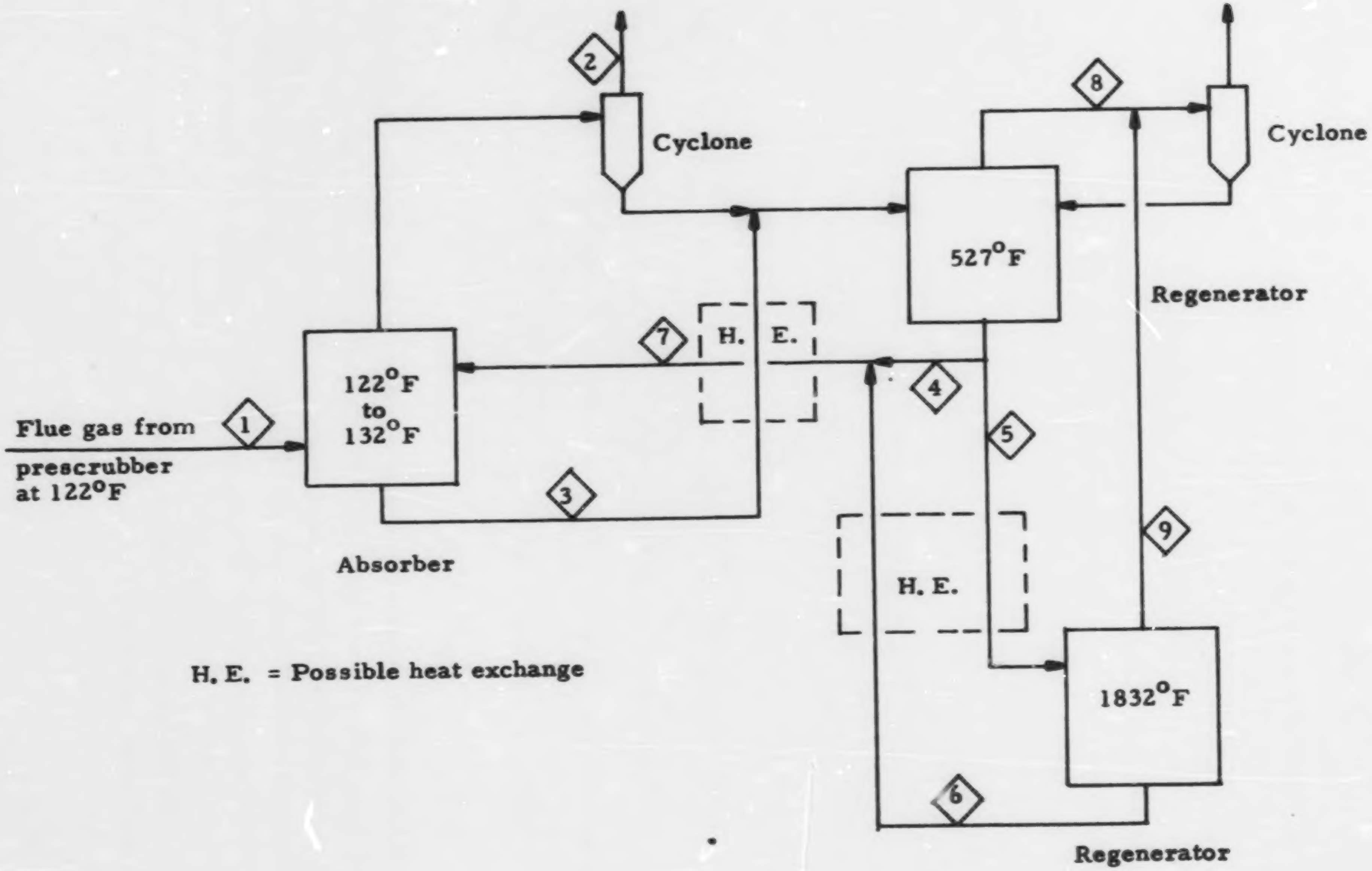
$$ZnSO_4 \cdot H_2O \xrightarrow{\Delta} ZnSO_4 + H_2O\uparrow \qquad (42)$$

Regenerator (1832°F):

$$ZnSO_4 \longrightarrow ZnO + SO_3\uparrow \qquad (39)$$

$$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2 \qquad (40)$$

The gas stream is first prescrubbed with water to remove fly ash and SO_2 to cool the gas to a temperature (122°F or 50°C) where absorption of the SO_2 by zinc oxide readily occurs, and to saturate the gas with water at this temperature as an aid in promoting SO_2 absorption. The SO_2 is then absorbed from Stream 1 at a slightly higher temperature in the zinc oxide fluidized bed absorber, and the purified gas, Stream 2, is vented. Some oxidation to sulfate may occur in the absorber, so that Stream 3 will consist of sulfite, sulfate, and unreacted oxide. Sulfate, at this point, will be in the form of the monohydrate, $ZnSO_4 \cdot H_2O$ (Reference 25).


Flue gas from
prescrubber
at 122°F
1
122°F
to
132°F
Absorber
2
Cyclone
3
7
H. E.
4
5
527°F
8
Cyclone
Regenerator
9
H. E.
1832°F
6
Regenerator

H. E. = Possible heat exchange

BLOCK FLOW DIAGRAM
FLUIDIZED BED ZINC OXIDE SYSTEM

Figure 4

Stream 3 enters a fluidized bed regenerator at 527°F (275°C). The steam required for promoting the decomposition is provided by the water of crystallization of both the sulfite, $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$, and the sulfate, $ZnSO_4 \cdot H_2O$. The gas, Stream 8, will consist only of SO_2 and water vapor. Most of the solids from the 527°F regenerator are returned to the absorber, as indicated by Stream 4.

Depending on the degree of oxidation in the absorber, a portion of the material calcined in the 527°F regenerator is further processed in a second regenerator at 1832°F (1000°C), as indicated by Stream 5. Both Streams 4 and 5 contain zinc oxide and anhydrous zinc sulfate, but little or no zinc sulfite.

The 1832°F regenerator may be fired either directly or indirectly. In the former case the combustion gases from a gas or oil burner would be utilized. At 1832°F, dissociation of SO_3 to SO_2 is complete, so that the gas, Stream 9, will consist of SO_2 and O_2 (indirect firing) or of SO_2, O_2, and combustion gases (direct firing). In either case, Stream 9 would probably be combined with Stream 8 to give an SO_2-rich gas suitable for SO_2 recovery.

The underflow from the 1832°F regenerator, Stream 6, consists only of zinc oxide. This is combined with Stream 4 to yield Stream 7, which contains zinc oxide and zinc sulfate, but little or no zinc sulfite. The zinc sulfate in the system will build up to an equilibrium value, which will be determined jointly by the amount of sulfate formed in the absorber (and the small amount possibly formed in the 527°F regenerator) and the amount of sulfate processed in the 1832°F regenerator.

The economics of the system shown in Figure 4 will depend largely on the amount of sulfate formed in the absorber. If this is small, the 1832°F regenerator will be relatively small, and the overall heat input to the system will not be excessive.

A further discussion of Figure 4 is presented in Part Six, Section III. A, and relates to the overall heat requirements for the system.

It may be noted that zinc is somewhat unique in that the sulfate is highly water soluble ($ZnSO_4$, 42 g/100 g H_2O at 0°C, 61 g/100 g at 100°; $ZnSO_4 \cdot H_2O$ reported as soluble at ambient temperature, 89.5 g/100 g at 100°, Reference 26, whereas the oxide and sulfite are both insoluble ZnO, 0.0042 g/100 g at 18°; $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$, 0.16 g/100 g at 25°). The possibility therefore exists of extracting the sulfate present in Stream 5 of Figure 4 with water. The extract could be further processed, particularly if the flue gas to be treated is derived from a zinc smelter, where zinc metal is normally produced through the electrolysis of aqueous zinc sulfate. The water extraction of zinc sulfate would eliminate the need for the 1832°F regenerator.

More recently, a system has been devised in which neither high temperature calcination nor leaching of the sulfate is required. The new system includes the use of ferrous ion in the prescrubber, so that oxidation in the absorber will be minimal. The absorption of SO_2 and regeneration of the oxide from the resulting sulfite are conducted in the manner described above, but any sulfate formed is removed from the system by simple filtration. This is accomplished by dissolving a portion of the sulfite-sulfate mixture in aqueous SO_2 and reprecipitating the sulfite with zinc oxide. The sulfate solution is then filtered, and the sulfite cake returned to the process. A discussion of the economics of this system is given in Part Six, Section III.

PART FIVE
OXIDATION AND NO_x STUDIES

I. INTRODUCTION

The scope of the work in Phase IV concerning oxidation and NO_x studies consisted of two separate tasks, one for each study (see Part One, Section I).

The purpose of the oxidation studies was to determine the degree to which inadvertent sorbent oxidation in aqueous scrubbers could be minimized by the utilization of various oxidation inhibitors and complexing agents both with and without fly ash being present in the flue gas being treated. Presuming that the degree of oxidation could not be economically reduced by the use of inhibitors or complexing agents, the technical feasibility of separating the oxidation product from the scrubber effluent by chemical or ion-exchange means was to be investigated, followed by the thermal, chemical, or electrochemical regeneration of the resultant material. Finally, the effects that pre-scrubbing has on the degree of oxidation in the main SO_2 scrubber were to be ascertained.

The NO_x studies were to include the determination of the degree of interference that inadvertent sorption of NO_x into SO_2 scrubbing solutions had on SO_2 removal efficiencies both with and without fly ash being present in the flue gas being tested. The technical feasibility of achieving high NO_x removal efficiencies in conjunction with high SO_2 removal efficiencies was to be assessed.

As the work progressed, it became evident that these tasks could be studied concurrently, especially since the NO_x in the flue gas (in the presence of O_2) was the major contributor to oxidation of SO_2 during its absorption. It is for this reason that the tasks have been combined into "Oxidation and NO_x Studies." The scope of these tasks was such that it was not possible to investigate all aspects in the laboratory.

Section II discusses the experimental program of the oxidation and NO_x studies. Description of equipment, operating procedure, analytical methods and calculations will be found in Appendix A.

II. EXPERIMENTAL RESULTS

A. LABORATORY EVALUATION OF INHIBITING AND COMPLEXING AGENTS

1. Introduction

The purpose of this work was the determination of the degree to which inadvertent oxidation in aqueous scrubbers can be minimized by the utilization of various oxidation inhibitors and complexing agents with and without fly ash being present in the flue gas.

The oxidation of aqueous solutions of salts of sulfurous acid in the presence of oxygen proceeds by a free radical chain mechanism (Reference 11); accordingly, compounds capable of breaking the reaction chain may serve as suitable inhibitors. Thus, the general class of free radical oxidation inhibitors were considered that finds wide applications in such diverse fields as rubber compounds, gasoline stabilization, and food technology. Another possible way of preventing oxidation by metal catalysis is by the use of complexing agents, of which there are many commercially available today. Only those candidates that have been found to be effective in various applications, and which are commercially available in production quantities, were investigated.

2. Screening Tests

The original plan was to screen the candidate materials in simple apparatus using a synthetic flue gas with fly ash added separately and at various levels, which would reflect the approximate degree of ash removal expected in the prescrubber, e.g. 95 and 98%. The candidate inhibitors and complexing agents were to be tested in this system at various concentrations. The test solutions were to be analyzed for sulfate formation and compared with the results obtained from suitable blank runs in which no agent was used. A reevaluation of this procedure showed that the desired results could probably be obtained with a simpler approach. Therefore, a test was substituted that involves the addition of air to the lean sodium sulfite-bisulfite solution (used in Johnstone's Zinc Oxide process - Reference 7). Fly ash and inhibitor or complexing agent were added in fixed, constant quantities. This procedure proved adequate, at least as a preliminary screening procedure, for the various inhibitors and complexing agents tested in the lean sodium sulfite-bisulfite solution with a pH of 6.5.

The test procedure consisted of the following:

100 ml of 0.65 S/C_a* absorbent (lean solution), which had been prepared using oxygen-free boiled distilled water, was transferred to a 3-neck 300 ml flask fitted with a reflux condenser and a thermometer. A nitrogen purge was applied, using a fritted glass gas-dispersion tube. The nitrogen purge was maintained while the contents of the flask were heated to 50°C (expected scrubber temperature). The nitrogen purge was stopped and air at the rate of 500 ml per minute was introduced for fifteen minutes through the gas-dispersion tube. The temperature of the lean solution was maintained at 50°C during the addition of air. The heat was removed and a nitrogen purge was maintained until the material cooled to room temperature. A 1 ml sample of the cooled solution was added to 10 ml of concentrated hydrochloric acid and the mixture evaporated to dryness on a 130°C oil bath. This procedure removed the sulfite from the solution. The residual dry material was dissolved in 100 ml of distilled water. The sulfate content of this solution was determined using the turbidimetric method.

Blank tests were made to check the oxidation of the solution both with and without the addition of fly ash. The effect of the addition of inhibitors or complexing agents on the oxidation of these systems was compared with the blank test results. A few tests were made using a combination of an inhibitor and a complexing agent. The materials - inhibitor and/or complexing agent and fly ash - were added in quantities of approximately 100 mg each. In the tests containing fly ash and/or insoluble inhibitor or complexing agent, it was necessary to filter the solution before adding it to the concentrated hydrochloric acid.

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* S/C_a used by Johnstone (Reference 7). See Appendix A, Section IV for discussion.

3. Experimental

Base line tests were made on the solution, after which tests with additions of fly ash, hydroquinone, and fly ash plus hydroquinone were completed. Approximately 100 mg quantities of fly ash and hydroquinone were added to the 300 ml of absorbent in these tests. The results of these tests are given in Table 15.

The preliminary tests indicate that:

- The solution as prepared under oxygen-free conditions contains a small amount of sulfate ion.
- Introduction of air will oxidize the sulfite.
- The addition of fly ash increases the extent of oxidation.
- Addition of hydroquinone immediately suppresses the oxidation due to the fly ash addition.

The inhibitors and complexing agents checked in the screening tests are given below.

Inhibitors tested were:

Hydroquinone, N, N'-dimethylformamide, N, N'-dimethylacetamide, N, N'-diphenyl-p-phenylenediamine, N, N'-di-β-naphthyl-p-phenylenediamine, N-phenyl-N'-cyclohexyl-p-phenylenediamine, N-phenyl-β-naphthylamine, butylated hydroxy toluene, butylated hydroxyanisole, 1, 1-thiobis-(2 naphthol), and N-phenyl-α-naphthylamine.

Complexing agents tested were:

Ethylenediaminetetraacetic acid, nitrilotriacetic acid, N, N'-disalicylidene-1, 2-propylendiamine (80% in toluene), diethylenetriaminepentaacetic acid pentasodium salt, and citric acid.

TABLE 15

BASE LINE INHIBITOR SCREENING TESTS

Sample No.	Hydroquinone mg	Fly Ash mg	$SO_4^=$, ppm in Absorbent	Wt-% SO_2 oxidized
Blank*	-	-	800	1.04
1	-	-	2600	3.38
2	100	-	1650	2.14
3	99	-	1900	2.47
Blank*	-	-	900	1.17
4	-	100	4500	5.84
5	100	100	1900	2.47
6+	101	101	1850	2.42
7+	101	101	1900	2.47

* The blank runs were on the absorbent solution as prepared and protected with N_2 atmosphere.

+ In these tests, the solution containing hydroquinone and fly ash was stirred for 23 hours under N_2 atmosphere in order to determine if it is necessary to allow the inhibitor extended time to react with the iron in the fly ash.

The test results are shown in Table 16. Analysis of the data indicates the following:

The lean solution, as prepared with boiled distilled water and protected with nitrogen atmosphere, shows a content of 800 - 950 ppm $SO_4^=$. This compares with 800 - 900 ppm $SO_4^=$ in the blank tests.

Introduction of air into this solution increased the $SO_4^=$ to 2700 ppm (see blank tests). The $SO_4^=$ content of the freshly prepared solution is due to either $SO_4^=$ present in the solid reagents or oxidation of $SO_3^=$ to $SO_4^=$ during the solution preparation, or both.

Hydroquinone was the best material tested, inhibiting the oxidation both with and without fly ash present (Tests 39 and 40). These results compare favorably with those reported in Table 15.

Nitrilotriacetic acid (Tests 29 and 30) and butylated hydroxyanisole dissolved in toluene (Tests 15 and 16) were next best in activity (a blank test to check the effect of toluene in a system containing fly ash showed no appreciable reduction in oxidation).

N, N'-disalicylidene-2-propylenediamine (80% solution in toluene) plus 2 ml toluene, (Tests 17 and 18), and ethylene-diaminetetra-acetic acid (Tests 27 and 28) both showed some activity in suppressing oxidation with fly ash present. No noticeable improvement was apparent in the systems not containing fly ash.

Other materials showing some reduction in oxidation with fly ash present but no reduction in fly ash-free solutions were: N-phenyl-N'-cyclohexyl-p-phenylenediamine (Tests 9 and 10); diethylenetriaminepentaacetic acid pentasodium salt (Tests 21 and 22); and N-phenyl-α-naphthylamine (Tests 23 and 24). Their activities were borderline under the test conditions used.

Two series of tests were made with combinations of an inhibitor and a complexing agent in order to determine if their oxidation suppression characteristics were additive. Tests 35 and 36, using hydroquinone and nitrilotriacetic acid, indicate that combining these materials

TABLE 16

INHIBITOR AND COMPLEXING AGENT SCREENING TESTS

Test No.	Additive*		Fly Ash mg	$SO_4^=$, ppm in Absorbent	Wt-% SO_2† oxidized	Remarks
	Name	mg				
1	DMF	101	-	3400	4.42	DMF = N, N'-dimethylformamide
2	DMF	98	99	4500	5.85	
3	DMA	105	-	4400	5.72	DMA = N, N'-dimethylacetamide
4	DMA	105	101	5000	6.50	
5	DPPD	100	-	4500	5.85	DPPD = N, N'-diphenyl-p-phenylene-diamine, insoluble
6	DPPD	101	101	5200	6.76	
7	DNPD	100	-	5000	6.50	DNPD = N, N'-di-β-naphthyl-p-phenylenediamine, insoluble
8	DNPD	101	101	5400	7.02	
9	PCPD	100	-	3000	3.90	PCPD = N-phenyl-N'-cyclohexyl-p-phenylenediamine, insoluble
10	PCPD	100	102	3200	4.16	
11	PNA-2	99	-	2200	2.86	PNA-2 = N-phenyl-β-naphthylamine
12	PNA-2	99	102	4100	5.33	
13	CaO-3	100	-	2600	3.38	CaO-3= butylated hydroxy toluene, insoluble. Dissolved in 2 ml toluene.
14	CaO-3	102	98	5900	7.67	
15	CaO-7	100	-	2200	2.86	CaO-7 = butylated hydroxyanisole, insoluble. Dissolved in 2 ml toluene.
16	CaO-7	100	102	2500	3.25	
Blank	-	-	-	950	1.24	Lean solution as prepared - no air.
Blank	-	-	102	4000	5.20	Added 2 ml toluene - added air.
17	DSPD	129	-	2500	3.25	DSPD = 80% sol N, N'-disalicylidene-1, 2-propylenediamine.
18	DSPD	123	99	2900	3.77	Added 2 ml toluene.
Blank	-	-	-	800	1.04	New lean solution - no air.
Blank	-	-	-	2700	3.51	New lean solution - added air.
19	CaO-30	103	-	4300	5.59	CaO-30 = 1, 1'-thiobis-(2-naphthol) insoluble. Dissolved in 2 ml toluene
20	CaO-30	104	99	4400	5.72	

TABLE 16 (cont'd)

Test No.	Additive* Name	Additive* mg	Fly Ash mg	SO$_4^=$, ppm in Absorbent	Wt-%, SO$_2$† oxidized	Remarks
21	DETPA	102	-	2600	3.38	DETPA = diethylenetriaminepentaacetic acid pentasodium salt, insoluble. Dissolved in 2 ml toluene.
22	DETPA	99	101	3300	4.29	
23	PNA-1	102	-	2900	3.77	PNA-1 = N-phenyl-α-naphthylamine insoluble. Dissolved in 2 ml toluene.
24	PNA-1	103	98	3200	4.16	
25	CA	103	-	2900	3.77	CA = citric acid
26	CA	101	102	4100	5.33	
27	EDTA	102	-	2600	3.38	EDTA = ethylenediaminetetraacetic acid.
28	EDTA	101	103	2900	3.77	
29	NTA	103	-	2000	2.60	NTA = nitrilotriacetic acid
30	NTA	101	104	2700	3.51	
31	Zn	103	-	4900	6.37	Zn = zinc dust
32	Zn	103	98	7800	10.14	
33	Zn	1103	-	25000	32.50	
34	Zn	25	102	6900	8.97	
35	HQ NTA	103 103	-	1900	2.47	HQ = hydroquinone
36	HQ NTA	103 102	102	1900	2.47	
37	CaO-7 NTA	99 98	-	1900	2.47	CaO-7 in 2 ml toluene
38	CaO-7 NTA	103 101	101	2100	2.73	CaO-7 in 2 ml toluene
39	HQ	102	-	1900	2.47	
40	HQ	99	102	1900	2.47	

* Inhibitor or complexing agent

† Refers to % of SO$_2$ available in the solution.

has no advantage over hydroquinone alone. In the case of the combination of butylated hydroxy anisole and nitrilotriacetic acid (Tests 37 and 38), a slight improvement is indicated (compared to the individual compounds) especially in the systems containing fly ash.

Zinc metal dust was tried on the basis of the electromotive series of metals, i.e., suppress the activity of iron. Tests 31 - 34 indicate, however, that zinc dissolves in the lean solution which is oxidized to zinc sulfate.

The effect of inhibitors on the oxidation of SO_2 in the standard apparatus used in the oxidation and NO_x studies is discussed in Section II. C.

B. BASE LINE TESTS IN BENCH SCALE UNIT

A series of runs was made in both the recirculating and in the once through scrubbers to establish the base line data on SO_2 removal efficiencies in this equipment. The data are given in Tables 17 and 18 and Figure 5.

The data in Table 17 were obtained in the recirculating scrubber by the method outlined in the operating and analytical procedures (see Appendix A). The first run was made with a gas mixture containing CO_2 in addition to SO_2 and nitrogen. The second run was made with SO_2 in nitrogen. In both runs the overhead gas composition was less than 0.015% SO_2 when the 0.85 S/C ratio was reached. The S/C ratios were calculated assuming there was no appreciable amount of oxidation of SO_2 to $SO_4^=$. The actual value of oxidation in the samples was not determined, but from all indications it was very low. The outlet gas composition vs. the S/C ratio in the solution has been plotted in Figure 5 for both runs. The data for both runs fall on a single curve. This indicates that the presence of CO_2 in the flue gas does not have a detrimental effect on the ability of the solution to absorb SO_2.

TABLE 17

BASE LINE OXIDATION STUDIES - RECIRCULATING SCRUBBER

Base line data with 0.9 in ID glass scrubber
packed with 32 inches of 0.5-in porcelain Intalox
saddles. Recirculating solution system.

Run No. 1

Inlet Gas: 5/0 liter/min with 0.3% SO_2 and 15% CO_2 in nitrogen

Time hours	Solution S/C $\frac{\text{moles } SO_2}{\text{moles } Na^+}$	Outlet Gas mole % SO_2	Solution Temp. °C	Solution Rate ml/min	Scrubber Gas ΔP mm H_2O
0	0.58	-	49	282	11
0.5	0.64	0.0004	50	282	11
1.0	0.69	0.0012	49	282	11
1.5	0.74	0.0022	50	282	11
2.0	0.79	0.0048	50	282	11
2.5	0.85	0.0087	50	318	12
3.0	0.91	0.0146	49	318	14

Run No. 2

Inlet Gas: 5.0 liter/min with 0.3% SO_2 in nitrogen

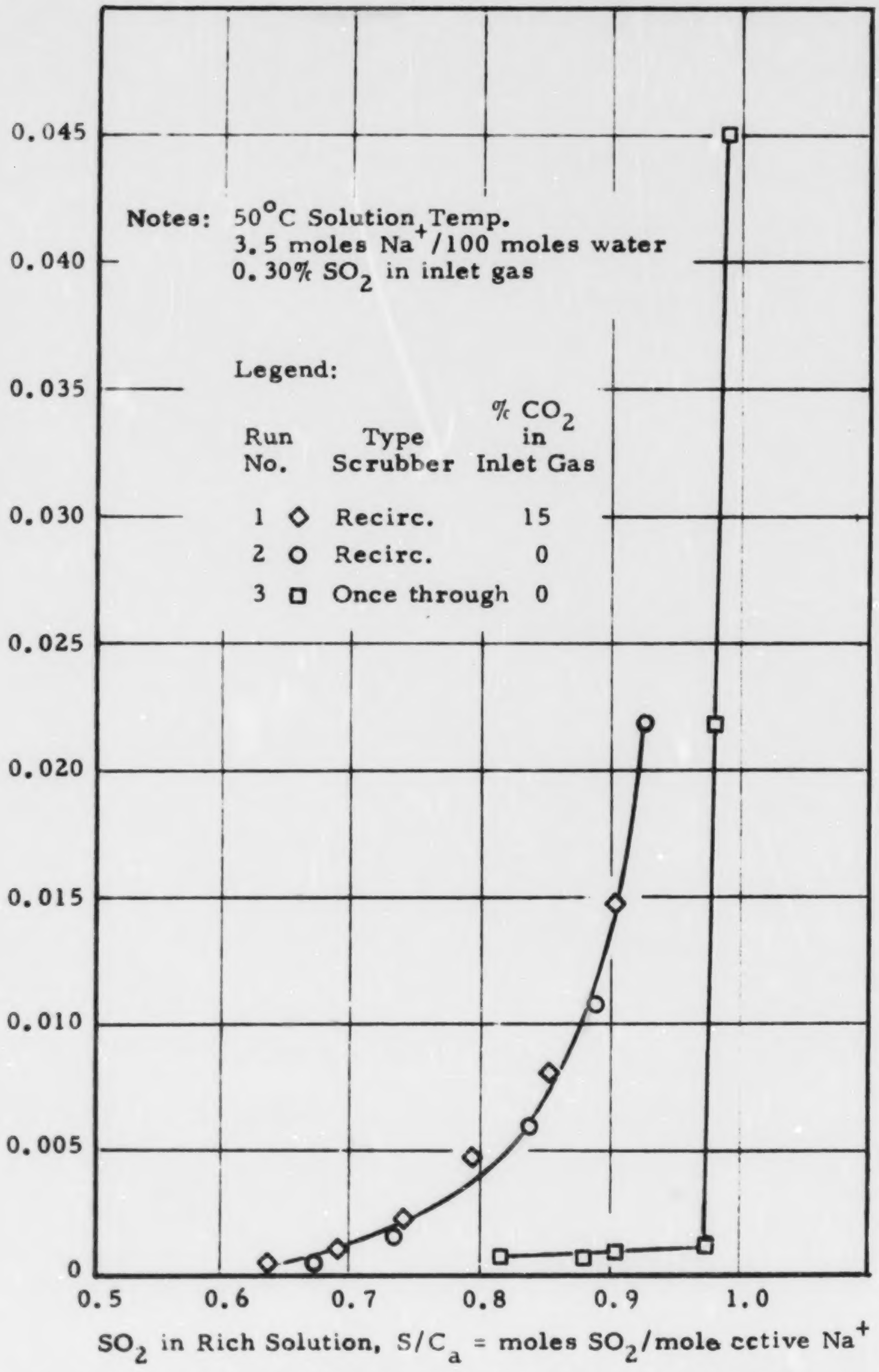
0.	0.58	-	51	275	12
0.5	0.64	0.0003	49	275	12
0.8	0.67	0.0006	50	275	12
1.4	0.74	0.0017	50	275	12
2.4	0.84	0.0061	50	275	12
2.8	0.89	0.0108	50	275	12
3.4	0.93	0.0220	50	275	12

TABLE 18

BASE LINE OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Base line data with a 0.2 in ID glass tube 10 ft long packed with a single Teflon helix. Once through solution system. Inlet gas: 5.0 liter/min with 0.3% SO_2 in nitrogen.

Time hours	Outlet Solution S/C $\frac{\text{moles } SO_2}{\text{moles } Na^+}$	Outlet Gas mole % SO_2	Solution Temp. °C	Lean Solution Rate ml/min	Scrubber Gas ΔP mm H_2O
0	-	0.0008	50	2.1	240
0.7	0.82	0.0008	50	1.8	245
1.0	-	0.0012	50	1.6	240
1.4	-	0.0010	50	1.6	235
1.8	0.88	0.0010	50	1.5	235
2.1	-	0.0012	50	1.4	300
2.3	0.91	0.0012	50	1.3	270
4.9	0.98	0.0012	50	1.0	260
5.5	0.99	0.0450	50	0.8	265
5.8	0.98	0.0218	50	0.9	265



% SO_2 IN SCRUBBER OUTLET GAS VS S/C OF RICH SOLUTION FOR RECIRCULATING SCRUBBER AND ONCE THROUGH SCRUBBER

Figure 5

Table 18 gives the data obtained in the once through scrubber. Lean solution containing 3.5 molal sodium with 0.65 S/C ratio was used in this run along with 5.0 liter/min gas - containing 0.3% SO_2 in nitrogen. This column turned out to be very efficient so that with the true countercurrent operation it was possible to reduce the liquid rate to the point where the S/C_a ratio in the rich solution approached 0.98 before the SO_2 content of the outlet gas became 0.015%. The relatively small inside diameter of the column combined with the swirling effect of the Teflon helix caused a relatively high pressure drop, which in turn was responsible for the good absorption efficiency.

C. OXIDATION AND NO_x EXPERIMENTS

1. Introduction

The results of the runs made in the once through scrubber are given in Table 19 while the recirculating scrubber test results are presented in Table 20. The tables provide all of the important information pertaining to each test. Oxidation of SO_2 to $SO_4^=$ is reported as a percent of the SO_2 in the entering flue gas.

The absorption system using 3.5 molal sodium sulfite-bisulfite with 0.65 S/C_a was investigated more than any other system. This absorbent is the same as that used in the Johnstone Zinc Oxide process.

2. Effect of O_2

Runs 1 and 2 (Table 19), which were made without O_2 and NO_x in the feed gas and with a 3.5 molal, 0.68 S/C_a sodium sulfite-bisulfite solution, showed no measurable oxidation. The presence of CO_2 in the feed gas affected neither the oxidation nor the absorption of SO_2.

Runs 3, 4, 8-1, 8-2, 14, and 16-1 were made with the same solution and with the addition of O_2 to the feed gas. These runs show a small but consistent oxidation of about 1% of SO_2 to $SO_4^=$ in the once through scrubber, which is believed to be due to the difficulty in preventing oxidation of the rich and lean solution samples during sampling and analysis.

TABLE 19

OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Run No.	Prescrubber Solution	Inlet Solution				Outlet Solution			Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to $SO_4^=$ %	Scrubber Gas ΔP mm H_2O	Sulfur Balance $\frac{Out}{In}$ %
		Composition	Rate ml/min	Moles/liter		S/C_a	Moles/liter		NO	NO_2				
				SO_2	$SO_4^=$		SO_2	$SO_4^=$						
1-1[a]	H_2O	3.5 molal Na[b] 0.68 S/C_a	1.72	1.26	0.009	0.88	1.63	0.010	0	0	0.0018	trace	186	101
1-2			1.69	1.26	0.009	0.89	1.65	0.009	0	0	0.0040	0	186	102
1-3			1.56	1.26	0.009	0.92	1.71	0.008	0	0	0.0022	negl.	185	103
1-4			1.45	1.26	0.009	0.93	1.73	0.009	0	0	0.0022	trace	175	103
2-1[c]	H_2O	3.5 molal Na 0.68 S/C_a	1.76	1.25	0.015	0.88	1.62	0.015	0	0	0.0010	negl.	186	101
2-2			1.68	1.25	0.015	0.90	1.66	0.014	0	0	0.0018	negl.	186	102
2-3			1.63	1.25	0.015	0.91	1.67	0.015	0	0	0.0010	negl.	184	103
2-4			1.57	1.25	0.015	0.91	1.68	0.016	0	0	0.0012	trace	184	102
2-5			1.47	1.25	0.015	0.94	1.72	0.016	0	0	0.0018	trace	188	104
3-1	H_2O	3.5 molal Na 0.66 S/C_a	1.70	1.20	0.026	0.90	1.62	n.d.	0	0	0.0014	n.d.	185	104
3-2			1.58	1.20	0.026	0.92	1.66	0.031	0	0	0.0014	1.5	188	104
3-3			1.56	1.20	0.026	0.90	1.64	0.026	0	0	0.0022	0.3	186	103
3-4			1.47	1.20	0.026	0.92	1.67	0.026	0	0	0.0022	0.3	182	103
4-1	H_2O	3.5 molal Na 0.66 S/C_a	1.48	1.20	0.027	0.92	1.67	0.030	0	0	0.0018	0.8	185	103
4-2			1.60	1.20	0.027	0.90	1.62	0.030	0	0	0.0018	0.8	185	102
4-3			1.70	1.20	0.027	0.89	1.61	0.031	0	0	0.0014	1.2	185	104
4-4			1.44	1.20	0.027	0.92	1.66	0.031	0	0	0.0014	1.0	184	102
5-1	H_2O	3.5 molal Na 0.67 S/C_a	1.52	1.21	0.032	1.03	1.36	0.275	400	400	n.d.	60.0	187	99
5-2			1.26	1.21	0.032	1.08	1.40	0.325	400	400	n.d.	60.0	187	100
5-3			1.66	1.21	0.032	1.00	1.37	0.250	400	400	n.d.	59.0	192	101
6-1	12.8% H_2SO_4[d]	3.5 molal Na 0.67 S/C_a	1.67	1.20	0.052	0.94	1.61	0.076	400	0	n.d.	7.1	185	104
6-2			1.84	1.20	0.052	0.91	1.56	0.074	400	0	n.d.	6.5	188	103
7-1	12.8% H_2SO_4	3.5 molal Na 0.66 S/C_a	1.91	1.21	0.013	0.96	1.51	0.127	0	120	n.d.	35.3	48	106
7-2			1.78	1.21	0.013	0.95	1.52	0.138	0	120	n.d.	36.0	48	105
7-3			1.68	1.21	0.013	0.98	1.57	0.134	0	120	n.d.	33.0	48	107

GENERAL NOTES: The feed gas consisted of 5 liters/min of 0.3 mole-% SO_2, 14.7 mole-% CO_2, 2.8 mole-% O_2 in N_2, except as noted, plus NO and NO_2 as indicated. The gas mixture was saturated with water at 50°C. The solution temperature was maintained at 50°C. The scrubber was a 0.20 in. ID x 10 ft tall glass tube with a 0.020 in. dia type 304 ss helix in Runs 1 to 6. The scrubber was changed to a 0.28 in. ID x 10 ft tall glass tube with a 0.033 in. OD Teflon tube helix beginning with Run 7. See Appendix A, Section IV, for explanation of columns "S/C_a," "Oxidation of SO_2 to $SO_4^=$", and "Sulfur Balance."

a. 0.3 mole-% SO_2 in N_2 in Run 1.

b. Na_2SO_3 - $NaHSO_3$ solution.

negl. Negligible

c. 0.3 mole-% SO_2, 14.7 mole-% CO_2 in N_2 in Run 2.

n.d. Not determined.

d. See Appendix A, Section II. B.

TABLE 19 (Cont'd)

OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Run No.	Prescrubber Solution	Inlet Solution				Outlet Solution			Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to SO_4 %	Scrubber Gas Δp mm H_2O	Sulfur Balance Out/In %
		Composition	Rate ml/min	Moles/liter SO_2	Moles/liter $SO_4^=$	S/C_a	Moles/liter SO_2	Moles/liter $SO_4^=$	NO	NO_2				
8-1	12.8% H_2SO_4	3.5 molal Na[b] 0.67 S/C_a	1.78	1.22	0.027	0.96	1.74	0.033	0	0	0.0017	1.6	55	105
8-2			2.17	1.22	0.027	0.93	1.63	0.035	0	0	0.0038	2.7	55	105
8-3[a]			2.22	1.22	0.027	0.91	1.64	0.035	0	0	0.0025	2.6	55	102
8-4[a]			2.08	1.22	0.027	0.95	1.71	0.034	0	0	0.0025	2.3	55	107
8-5[a]			1.52	1.22	0.027	1.04	1.87	0.037	0	0	0.0029	2.4	55	109
9-1	H_2O	3.5 molal Na 0.65 S/C_a	1.90	1.21	0.048	0.92	1.66	0.125	0	25	0.0025	20.0	44	102
9-2			2.30	1.21	0.048	0.87	1.55	0.121	0	25	0.0025	24.0	46	102
9-3			3.10	1.21	0.048	0.83	1.46	0.094	0	25	0.0021	21.0	54	101
9-4[c]			2.21	1.21	0.048	0.88	1.58	0.110	0	25	0.0025	20.0	45	101
10-1	H_2O	3.5 molal Na 0.65 S/C_a	2.94	1.27	0.009	0.76	1.58	0.033	475	0	0.0017	9.3	45	94
10-2			1.65	1.27	0.009	0.88	1.81	0.049	475	0	0.0029	8.9	46	97
10-3			2.20	1.27	0.009	0.84	1.67	0.042	475	0	0.0017	10.0	44	99
10-4[c]			2.10	1.27	0.009	0.85	1.70	0.040	475	0	0.0021	9.0	44	99
11-1	H_2O	3.5 molal Na 0.65 S/C_a	3.05	1.25	0.017	0.81	1.53	0.045	475	25	n.d.	12.5	45	101
11-2			1.60	1.25	0.017	0.97	1.80	0.081	475	25	0.0033	14.8	45	103
11-3			2.20	1.25	0.017	0.85	1.59	0.061	475	25	0.0025	15.3	46	105
11-4[c]			2.20	1.25	0.017	0.86	1.60	0.059	475	25	0.0025	13.8	46	102
12-1	H_2O	3.5 molal Na 0.65 S/C_a	2.35	1.25	0.017	0.87	1.55	0.088	450	50	0.0025	25.6	46	103
12-2			2.20	1.25	0.017	0.88	1.57	0.091	450	50	0.0016	24.8	46	106
13-1	H_2O	3.5 molal Na 0.65 S/C_a	2.05	1.22	0.034	0.76	1.44	0.082	0	25	0.0033	13.0	45	89
13-2			2.30	1.22	0.034	0.76	1.50	0.079	0	25	0.0025	12.7	45	90
14-1	H_2O	Same as 13	2.14	1.23	0.040	0.81	1.67	0.040	0	0	0.0025	0.0	45	96
15-1	H_2O	3.5 molal Na 0.65 S/C_a	2.06	1.23	0.042	0.87	1.49	0.057	450	0	0.0029	5.3	47	99
15-2			2.10	1.23	0.042	0.87	1.49	0.081	450	25	0.0029	13.3	46	101
15-3			2.07	1.23	0.042	0.88	1.47	0.104	450	50	0.0021	20.8	46	100
15-4			2.02	1.23	0.042	0.91	1.44	0.144	450	100	0.0021	33.4	46	101
15-5			1.96	1.23	0.042	0.95	1.38	0.208	450	240	0.0017	52.5	46	100
16-1[d]	H_2O	3.5 molal Na 0.65 S/C_a	2.07	1.22	0.038	0.83	1.47	0.043	0	0	0.0035	1.8	43	97
16-2[d]			2.15	1.22	0.038	0.84	1.47	0.066	0	25	0.0035	9.7	44	100
16-3[d]			2.19	1.22	0.038	0.84	1.46	0.068	470	25	0.0035	13.8	44	100
16-4[d]			2.15	1.22	0.038	0.86	1.46	0.090	470	50	0.0040	17.9	44	100

See Sheet 1 for General Notes.

a. Approximately 24 mg/min fly ash was added to the gas stream entering prescrubber. Analysis of gas leaving prescrubber indicated that about 95% of the fly ash was removed in the prescrubber.

b. Na_2SO_3 - $NaHSO_3$ solution.

c. Fly ash approximately 0.2 wt-% of the feed gas was added to gas entering prescrubber. About 95% of the fly ash was removed in the prescrubber.

n.d. Not determined

d. Inlet solution contained 40 ppm iron added as $Fe_2(SO_4)_3$.

TABLE 19 (Cont'd)

OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Run No.	Prescrubber Solution	Inlet Solution				Outlet Solution			Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to $SO_4^=$ %	Scrubber Gas Δp mm H_2O	Sulfur Balance $\frac{Out}{In}$ %
		Composition	Rate ml/min	Moles/liter		S/C_a	Moles/liter		NO	NO_2				
				SO_2	$SO_4^=$		SO_2	$SO_4^=$						
17-1	H_2O	3.5 molal Na 0.65 S/C_a and 13 ppm iron as $Fe_2(SO_4)_3$	2.06	1.26	0.018	0.87	1.52	0.063	470	30	0.0025	14.8	46	100
17-2[a]			2.06	1.26	0.018	0.87	1.51	0.063	470	30	0.0030	15.1	45	100
17-3[b]			2.10	1.26	0.018	0.88	1.53	0.064	470	30	0.0025	15.6	45	101
17-4[c]			2.12	1.26	0.018	0.87	1.52	0.063	470	30	0.0030	15.5	45	101
18-1[d]	H_2O	3.5 molal Na 0.65 S/C_a and 30 ppm iron as $Fe_2(SO_4)_3$	2.17	1.15	1.980	0.87	1.42	1.980	470	30	0.0041	2.0	45	100
18-2[d]			2.74	1.15	1.980	0.84	1.37	1.980	470	30	0.0040	2.0	45	100
18-3[d]			2.19	1.15	1.980	0.87	1.42	1.980	0	0	0.0055	2.0	44	100
19-1	H_2O	3.5 molal Na 0.65 S/Ca and 250 g NaCl/liter	2.36	1.11	0.021	0.83	1.336	0.048	470	30	0.0050	10.3	45	99
19-2			2.36	1.11	0.021	0.84	1.356	0.046	470	30	0.0060	9.5	45	100
19-3			2.60	1.11	0.021	0.82	1.311	0.046	470	30	0.0050	10.4	48	100
20-1	H_2O	7.0 molal Na 0.65 S/C_a	2.10	2.41	0.018	0.74	2.71	0.036	470	30	0.0060	6.4	47	101
20-2			1.50	2.41	0.018	0.78	2.86	0.047	470	30	0.0080	6.9	47	100
20-3			1.03	2.41	0.018	0.85	3.08	0.055	470	30	0.0090	6.3	46	104
21-1	H_2O	10.5 molal Na 0.65 S/C_a	1.37	3.52	0.021	0.70	3.71	0.172	470	30	0.0140	33.0	46	98
21-2			1.14	3.52	0.021	0.72	3.87	0.130	470	30	0.0140	20.0	46	98
21-3			0.53	3.52	0.021	0.86	4.54	0.166	470	30	0.0280	12.0	45	100
22-1	5.5% $FeSO_4$ and 7.0% H_2SO_4	3.5 molal Na 0.65 S/C_a	2.63	1.18	0.075	0.82	1.40	0.086	470	30	0.0040	4.4	47	99
22-2			2.14	1.18	0.075	0.85	1.44	0.090	470	30	0.0050	5.0	47	99
22-3			1.65	1.18	0.075	0.93	1.55	0.094	470	30	0.0060	5.0	47	101
23-1	5.5% $FeSO_4$ and 2.0% H_2SO_4	3.5 molal Na 0.65 S/C_a	2.80	1.15	0.025	0.77	1.36	0.038	470	30	0.0030	5.8	47	100
23-2			2.13	1.15	0.025	0.81	1.43	0.044	470	30	0.0030	6.6	48	98
23-3			1.51	1.15	0.025	0.90	1.57	0.053	470	30	0.0030	6.9	48	98
24-1[e]	5.5% $FeSO_4$ and 2.0% H_2SO_4	3.5 molal Na 0.65 S/C_a	2.74	1.12	0.054	0.77	1.31	0.071	470	30	0.0040	7.4	34	99
24-2[e]			2.10	1.12	0.054	0.83	1.41	0.073	470	30	0.0040	6.5	34	100
24-3[e]			1.53	1.12	0.054	0.90	1.51	0.082	470	30	0.0060	6.9	35	101
24-4[e]			1.19	1.12	0.054	0.98	1.64	0.085	470	30	0.0100	5.8	34	102

See Sheet 1 for General Notes.

[a] Inlet solution also contained 10 ppm hydroquinone.

[b] Inlet solution also contained 100 ppm hydroquinone.

[c] Inlet solution also contained 1000 ppm hydroquinone.

[d] Inlet solution also contained 26 g Na_2SO_4/100 ml.

[e] Scrubber length was only 5 feet.

TABLE 19 (Cont'd)

OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Run[a] No.	Prescrubber[b] Solution	Inlet Solution				Outlet Solution			Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to SO_4 %	Scrubber Gas Δp mm H_2O	Sulfur Balance $\frac{Out}{In}$ %
		Composition	Rate ml/min	Moles/liter		S/C_a	Moles/liter		NO	NO_2				
				SO_2	$SO_4^=$		SO_2	$SO_4^=$						
25-1	5.5% $FeSO_4$ and 7.0% H_2SO_4	7.0 molal K[c] 0.65 S/C_a	2.53	2.18	0.040	0.69	2.37	0.042	470	30	0.0030	0.8	34	98
25-2			1.80	2.18	0.040	0.73	2.48	0.047	470	30	0.0040	2.1	32	98
25-2			1.10	2.18	0.040	0.79	2.67	0.053	470	30	0.0060	2.3	32	98
26-1	5.5% $FeSO_4$ and 7.0% H_2SO_4	7.0 molal K 0.65 S/C_a No helix[a] in scrubber	1.63	2.18	0.075	0.75	2.51	0.080	470	30	0.0520	1.4	15	99
26-2			3.49	2.18	0.075	0.70	2.33	0.078	470	30	0.0390	1.8	17	99
26-3[d]			1.64	2.18	0.075	0.73	2.42	0.080	470	30	0.0310	1.3	12	98
26-4[e]			1.60	2.18	0.075	0.71	2.36	0.080	470	30	0.0100	2.9	4	101
27-1	5.5% $FeSO_4$ and 7.0% H_2SO_4	3.5 molal Na 0.55 S/C_a	1.32	1.04	0.025	0.82	1.48	0.031	470	30	0.0080	1.5	32	99
27-2			1.20	1.04	0.025	0.89	1.60	0.033	470	30	0.0090	1.6	32	103
27-3			1.04	1.04	0.025	0.94	1.66	0.046	470	80	0.0120	3.5	34	103
27-4[f]			0.94	1.04	0.025	0.98	1.74	0.048	470	80	0.0170	3.6	34	105
28-1	5.5% $FeSO_4$ and 7.0% H_2SO_4	10.5 molal K 0.50 S/C_a	1.35	2.55	0.026	0.58	2.61	0.312	470	30	0.0080	62.2	32	96
28-2			1.04	2.55	0.026	0.64	2.71	0.437	470	30	0.0080	68.9	34	99
28-3			0.76	2.55	0.026	0.67	3.10	0.271	470	30	0.0080	29.8	32	99
28-4			0.48	2.55	0.026	0.80	3.62	0.292	470	30	0.0150	20.6	32	101
28-5[g]			0.96	2.55	0.026	0.63	3.15	0.071	470	30	0.0050	6.9	33	101
29-1[g]	5.5% $FeSO_4$ and 7.0% H_2SO_4	10.5 molal K 0.57 S/C_a	0.99	2.81	0.093	0.68	3.28	0.146	470	30	0.0040	8.4	34	95
29-2[g]			0.69	2.81	0.093	0.76	3.61	0.177	470	30	0.0050	9.3	34	99
29-3[g]			0.46	2.81	0.093	0.85	4.03	0.188	470	30	0.0060	6.9	34	99
30-1[b]	7% H_2SO_4	3.5 molal K 0.65 S/C_a	2.00	1.16	0.028	0.81	1.44	0.028	0	0	0.0210	0.0	50	98
30-2[b, g]			2.45	1.16	0.028	0.76	1.37	0.028	0	0	0.0040	0.0	35	97
30-3[b, g]			2.72	1.16	0.028	0.76	1.34	0.045	470	30	0.0220	7.8	35	98
30-4[b, g]			2.81	1.16	0.028	0.76	1.29	0.083	400	400	0.0220	25.0	38	98
31-1[b, e]	7% H_2SO_4	3.5 molal K 0.65 S/C_a	2.63	1.14	0.032	0.70	1.26	0.039	0	0	0.0250	2.7	35	92
31-2[b]			2.46	1.14	0.032	0.75	1.33	0.054	470	30	0.0250	8.5	35	95
31-3[b]			2.47	1.14	0.032	0.75	1.23	0.120	400	400	0.0190	32.5	35	95
31-4[b, h]			2.86	1.14	0.032	0.74	1.21	0.123	400	400	0.0190	42.0	38	96
32-1	No prescrubber	7.0 molal K 0.65 S/C_a	1.51	2.21	0.040	0.70	2.38	0.045	0	0	0.0210	1.3	35	95
32-2[g]			1.43	2.21	0.040	0.72	2.44	0.045	0	0	0.0170	1.1	35	94
32-3[g]			1.55	2.21	0.040	0.73	2.45	0.078	470	30	0.0170	9.7	35	97
32-4[g]			1.50	2.21	0.040	0.75	2.28	0.228	400	400	0.0170	45.7	35	95

See Sheet 1 for General Notes.

a. Scrubber height reduced to 5 ft in all runs.

b. Prescrubber packed with 32 in. of 1/4 in. Intalox saddles.

c. K_2SO_3 - $KHSO_3$ solution.

d. Feed gas rate reduced to 3.87 liters/min.

e. Feed gas rate reduced to 2.25 liters/min.

f. Inlet solution contained 100 ppm hydroquinone.

g. Inlet solution contained 100 ppm nitrilotriacetic acid.

h. Inlet solution contained 200 ppm nitrilotriacetic acid.

TABLE 19 (Cont'd)

OXIDATION STUDIES - ONCE THROUGH SCRUBBER

Run[a] No.	Prescrubber Solution	Inlet Solution				Outlet Solution			Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to $SO_4^=$ %	Scrubber Gas ΔP mm H_2O	Sulfur Balance $\frac{Out}{In}$ %
		Composition	Rate ml/min	Moles/liter		S/C_a	Moles/liter		NO	NO_2				
				SO_2	$SO_4^=$		SO_2	$SO_4^=$						
33-1	No prescrubber	3.5 molal Na 0.65 S/C_a	1.94	1.24	0.021	0.92	1.67	0.021	0	0	0.0210	0.0	36	109
33-2[b]			1.90	1.24	0.021	0.92	1.68	0.021	0	0	0.0160	0.0	36	107
33-3[b]			1.97	1.24	0.021	0.95	1.64	0.064	420	30	0.0160	13.5	36	108
33-4[b]			1.88	1.24	0.021	0.86	1.24	0.208	400	400	0.0160	56.8	37	92
34-1	No prescrubber	7.0 molal Na 0.65 S/C_a	1.20	2.43	0.009	0.73	2.71	0.009	0	0	0.0270	0.0	37	93
34-2[b]			1.61	2.43	0.009	0.68	2.51	0.009	0	0	0.0120	0.2	37	90
34-3[b]			1.56	2.43	0.009	0.69	2.49	0.048	470	30	0.0130	9.7	36	91
34-4[b]			1.54	2.43	0.009	0.73	2.40	0.223	400	400	0.0130	53.0	36	93
35-1	No prescrubber	7.0 molal Na 6.5 S/C_a	0.90	2.38	0.064	0.84	2.94	0.109	470	30	0.0180	6.6	55	98
35-2			1.25	2.38	0.064	0.78	2.48	0.271	400	400	0.0060	42.0	55	94
35-3			1.40	2.38	0.064	0.70	2.09	0.366	400	400	0.0060	68.0	56	100
36-1	No prescrubber	0.5 N NaOH	2.61	n.a.	n.a.	0.25	0.13	0.114	400	400	0.0000	48.0	52	101
36-2			3.67	n.a.	n.a.	0.14	0.07	0.073	400	400	0.0000	43.0	57	85
37-1	No prescrubber	5.0 N NaOH	1.36	n.a.	n.a.	0.10	0.51	0.001	0	0	0.0000	0.2	52	100
37-2[c]			1.39	n.a.	n.a.	0.07	0.36	0.063	400	400	0.0000	14.1	52	98
37-3			1.41	n.a.	n.a.	0.06	0.29	0.137	400	400	0.0000	31.3	53	96
37-4			1.41	n.a.	n.a.	0.08	0.40	0.035	470	30	0.0000	8.1	53	99
38-2	No prescrubber	5.0 N NaOH	1.41	n.a.	n.a.	0.06	0.27	0.130	400	400	0.0000	31.0	56	96

See Sheet 1 for General Notes.

a. Scrubber height reduced to 5 ft in Runs 33, 34, and 35.

b. Inlet solution contained 100 ppm butylated hydroxy anisole.

n.a. Not applicable.

c. 0% oxygen in feed gas.

TABLE 20

OXIDATION STUDIES - RECIRCULATING SCRUBBER

Run No.	Circulating Solution							Inlet Gas ppm		Outlet Gas mole % SO_2	Oxidation of SO_2 to $SO_4^=$ %	Sulfur Balance Out/In %	Elapsed Time min.
			Solution at Start		Solution at End								
			Moles/liter		Moles/liter								
	Composition	Rate ml/min	SO_2	$SO_4^=$	SO_2	$SO_4^=$	S/C_a	NO	NO_2				
1-4	$Fe_2(SO_4)_3$ = 28 ppm Fe[a]	250	1.17	0.018	1.350	0.036	0.76	0	0	0.015	6.9	103	120
2-4	5 g fly ash = 16 ppm Fe[a]	250	1.20	0.025	1.420	0.042	0.80	0	0	0.013	6.4	100	120
3-4	5 ppm iron from fly ash[a]	250	1.16	0.025	1.350	0.040	0.76	0	0	0.012	5.5	99	120
4-2	$Fe_2(SO_4)_3$ = 100 ppm Fe[a,b]	250	1.15	0.033	1.390	0.048	0.78	0	0	0.013	5.8	99	120
5-2	5 ppm Fe residue[a]	250	1.18	0.038	1.370	0.044	0.77	0	0	0.013	2.4	100	120
6-2	7 ppm Fe residue[a]	250	1.14	0.049	1.270	0.143	0.87	480	30	0.024	38.0	100	120
7-2	2.5 wt-% $Mg(OH)_2$	400	n.a.	n.a.	0.093	0.015	0.82	0	0	0	11.8	87	60
7-3		350	n.a.	n.a.	0.008	0.120	0.94	400	400	0	96.7	102	60
8-1[c]	2.5 wt-% $Mg(OH)_2$	350	n.a.	n.a.	0.070	0.024	0.67	400	400	0	18.0	71[d]	60
8-2		350	n.a.	n.a.	0.066	0.035	0.71	470	30	0	38.0	82[d]	60
9-1	2.5 wt-% $Ca(OH)_2$	300	n.a.	n.a.	0.072	0.003	0.74	0	0	0	2.4	61[d]	60
9-2		300	n.a.	n.a.	0.041	0.051	0.82	400	400	0	38.0	72[d]	60
9-3	-	300	n.a.	n.a.	0.083	0.003	0.85	470	30	0	2.4	70[d]	60
10-1	5 N NaOH	400	n.a.	n.a.	0.088	0.017	0.02	470	30	0	14.8	93	60
10-2		400	n.a.	n.a.	0.104	0.102	0.02	400	400	0	68.0	90	60

General Notes: The feed gas consisted of 5 liters/min of 0.3 mole-% SO_2, 14.7 mole-% CO_2, 2.8 mole-% O_2 in N_2 except as noted, plus NO and NO_2 as indicated. The gas mixture was saturated at 50°C in a prescrubber containing water. The solution temperature was maintained at 50°C. The scrubber was a 7/8 in. ID x 3 ft tall glass tube packed with 32 in. of 1/2 in. ceramic Intalox saddles. See Appendix A, Section IV, for explanation of columns "S/C_a," "Oxidation of SO_2 to $SO_4^=$," and "Sulfur Balance."

a. Composition of the circulating solution consisted of 3.5 molal Na_2SO_3 - $NaHSO_3$ with an S/C_a = 0.65 plus additives as shown.

b. 1000 ppm hydroquinone added.

c. No O_2 in feed gas.

d. Some of the solids were held up on the packing, making an exact material balance impossible.

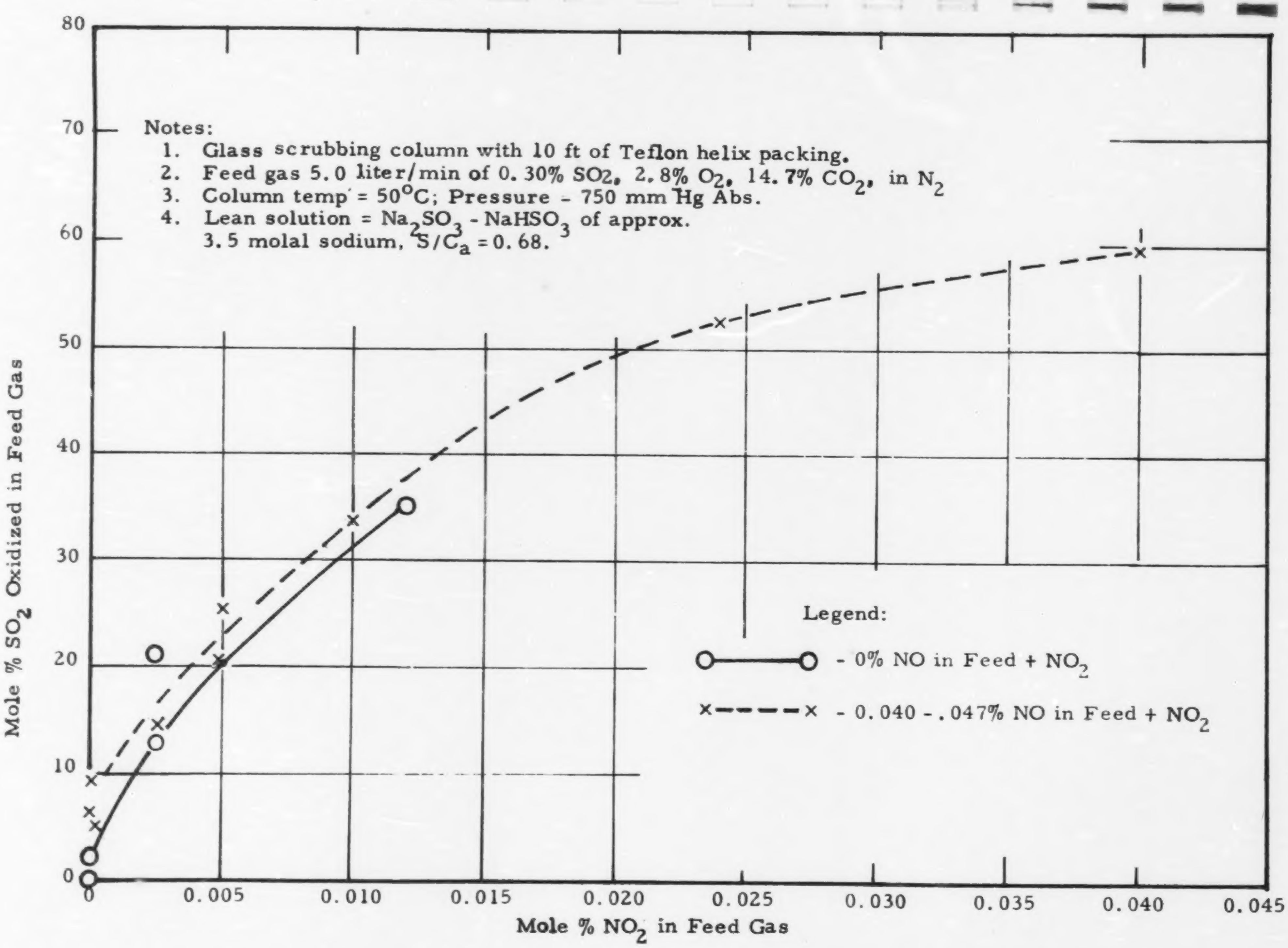
n.a. Not applicable.

3. Effect of NO_x and 2.8% O_2

Runs 5 through 15 were made in order to determine the effect of NO_x in the presence of O_2 upon the extent of oxidation in the once through scrubber with the 3.5 molal, 0.65 S/C_a sodium sulfite-bisulfite solution. The results of these runs have been plotted in Figure 6. Two series of runs were made in order to cover all ratios of NO/NO_2 of interest - the first series without NO but with increasing amounts of NO_2, and the second series with the normal range of NO and increasing quantities of NO_2. The first series of runs (plotted as a solid line on Figure 6) shows slightly less oxidation than the second series (dotted line). In both curves, the percent of NO_2 in the feed gas was controlled with the percent oxidation as the dependent variable. The data show that the NO_2 in the scrubber feed gas caused the large increase in SO_2 oxidation rate. Some of the NO was known to be oxidized to NO_2 in the prescrubber and in the line between the prescrubber and scrubber; otherwise, the two lines might have been identical.

4. Effect of Fly Ash

Three runs were made in which the feed gas to the once through scrubber contained appreciable quantities of fly ash (Runs 9-4, 10-4, and 11-4). During these runs, fly ash, approximating 0.2 wt.-% of the feed gas, was added to the prescrubber feed. The prescrubber for these runs had been modified so that only about 95% of the fly ash was removed in the prescrubber. The lean solution in these runs was the standard 3.5 molal sodium solution that had not been in contact with fly ash. A comparison of the amount of oxidation experienced in Samples 9-4, 10-4, and 11-4 with the oxidation experienced in the same runs (Samples 1-3) with no fly ash in the feed gas, shows that within the limits of error there was no change in the level of oxidation. It should be assumed, however, that in plant operations the solution would be recycled and would gradually accumulate an increasing concentration of fly ash or some ingredients from the fly ash that might greatly affect the extent of oxidation.



Notes:

1. Glass scrubbing column with 10 ft of Teflon helix packing.
2. Feed gas 5.0 liter/min of 0.30% SO_2, 2.8% O_2, 14.7% CO_2, in N_2
3. Column temp = 50°C; Pressure - 750 mm Hg Abs.
4. Lean solution = Na_2SO_3 - $NaHSO_3$ of approx. 3.5 molal sodium, $S/C_a = 0.68$.

EFFECT OF NO_x ON OXIDATION OF SO_2 TO $SO_4^=$ IN ONCE THROUGH SCRUBBER

Figure 6

One run was made to check this effect in the recirculating scrubber. In Run 2 (Table 20), the lean solution was shaken for 15 minutes with 5 g fly ash per liter and then decanted from the fly ash before adding the solution to the scrubber. This resulted in 16 ppm iron in the solution. Comparing this run with Run 3, in which the lean solution had not been in contact with fly ash, but 5 ppm iron was added as a salt, shows that oxidation had increased only slightly due to the higher iron content. This is an insignificant increase in oxidation when compared to the 3 to 4-fold increase found in the inhibitor screening tests (see Table 16). In the latter tests, about 0.1 g of fly ash was added directly to 100 ml of the lean solution and the oxidation increased from about 1 to about 5% based on the SO_2 in solution. In this case perhaps it was the large surface of the fly ash and possibly the oxygen adsorbed on the fly ash that caused the large increase in oxidation.

5. Effect of Ferric Ions in Solution

Runs 3, 4 and 16 (Table 19) made in the once through scrubber indicated that 40 ppm iron in the solution did not materially increase the level of oxidation. This was rather surprising, since many investigators have reported that iron is a mild oxidizing catalyst in sulfite solutions.

A series of tests was made in the recirculating scrubber to check the effect of various iron concentrations on oxidation.

Runs 1, 2, 3 and 4 (Table 20) were made in the recirculating scrubber with increasing quantities of iron added to the lean solution and no NO_x in the feed gas. Results showed about 25% increase in oxidation as the iron concentration was increased from 5 to 28 ppm. The accuracy of the oxidation value obtained for Run 4 (100 ppm iron) is doubtful, since a dark solid precipitated from the rich solution. These results indicate that the presence of iron in the sulfite solution may increase the oxidation 25% or more when absorbing SO_2 from gases containing O_2 but no NO_x.

6. Effect of Inhibitors

Several inhibitors, namely hydroquinone, nitrilotriacetic acid (NTA) and butylated hydroxy anisole (CaO-7)*, were found to be effective in lowering the extent of sulfite oxidation in the inhibitor screening tests. These tests were made with O_2 but with no NO_x present. Tests made in the once through scrubber showed that these inhibitors were not effective in most cases when NO_x was present. The exceptions to this statement were the runs with 10.5 molal potassium sulfite-bisulfite solution and NTA inhibitor (see Runs 28 and 29, Table 19). In this case, the inhibitor lowered the oxidation from a maximum of 69% to 7%, with the normal 95/5 ratio of NO/NO_2 present in the feed gas. In these runs, the effectiveness of the NTA inhibitor is believed to be due to the high pH of the solution. The pH of the 10.5 molal 0.5 S/C_a potassium solution in Run 28 was 12.6 compared to a 6.5 pH of the 3.5 molal 0.65 S/C_a sodium solutions. However, the NTA was not able to lower the level of oxidation below 7-9% in Run 29 where the lean solution pH was 7.5.

Runs 17 and 27 (Table 19) made with 0.001-0.10% hydroquinone in the presence of NO_x failed to suppress the oxidation. Runs 31 and 34 (Table 19) made with CaO-7 inhibitor also did not lower the oxidation rate in the presence of NO_x.

Since the recirculating scrubber was found to produce a higher level of oxidation than the once through scrubber (discussed later) it was logical to use this scrubber to test the effectiveness of hydroquinone as an oxidation inhibitor in the absence of NO_x. Comparing Runs 3 and 5 (Table 20) it can be seen that in the absence of NO_x addition of hydroquinone lowered the oxidation rate a little over 50%.

7. Effect of High Concentrations of Na_2SO_4 and NaCl

Run 18 (Table 19) was conducted with a feed solution that contained 26 grams of anhydrous sodium sulfate per 100 ml of the normal stock sulfite-bisulfite solution. The resulting solution was found to be slightly supersaturated at 25°C, but less than saturated at 50°C which is the temperature normally employed for absorption. The data for Run 18 clearly indicate that oxidation is markedly inhibited at high sulfate concentrations both in the absence and presence of NO_x. This can be explained in terms of the very limited solubility of oxygen in aqueous solutions at high ionic strength, and the supposition that little or no oxidation occurs in the gas phase. The observed inhibition of oxidation was tried by employing other soluble salts, such as sodium chloride. Here, however, with 250 g NaCl/liter (Run 19) the effect was not as great.

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* CaO-7 is trade name of Ashland Chemical Co.

The results obtained with sodium sulfate may be of value in connection with the Johnstone Zinc Oxide process, in which oxidation in the scrubber normally occurs to the extent of 10% or more. It would be required, however, that the precipitation of zinc sulfite through addition of zinc oxide to the rich scrubber solution not be accompanied by co-precipitation of sulfate.

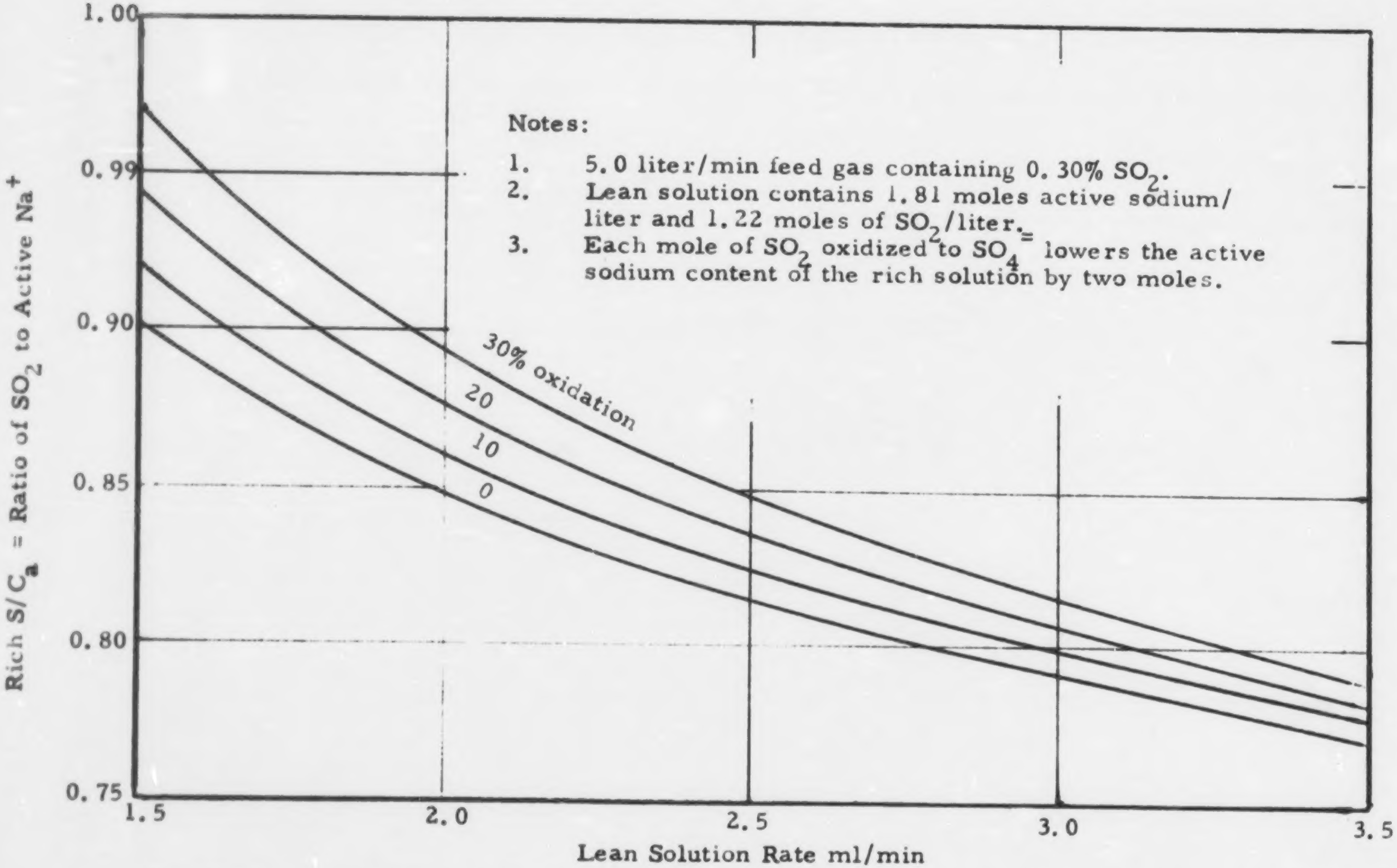
8. Effect of Oxidation of SO_2 on Required Solution Rate

In order to aid in selecting the proper lean solution rates for experimental runs, calculations were made to show how oxidation of SO_2 to $SO_4^{=}$ in the scrubber affects the rich solution S/C_a ratio. In Johnstone's work, a 0.85 S/C_a was used for design purposes, and in a commercial plant it is believed that this may be the highest practical ratio that will maintain less than 150 ppm SO_2 in the outlet gas.

Figure 7 illustrates how the lean solution rate must be increased at a given rich solution S/C_a as the oxidation level increases. For example, at 0.85 S/C_a, the solution rate must be increased from 2.0 ml/min at no oxidation to 2.45 ml/min at 30% oxidation.

9. Effect of Solution Flow Rate

The effect of solution rate on the extent of oxidation in the once through scrubber can be seen from Figures 8 and 9. With the exception of the 10.5 molal concentrations, there was almost no change in oxidation with solution rate for either the sodium or potassium sulfite-bisulfite solution. The 10.5 molal solution for both sodium and potassium solutions showed a rapid increase in the oxidation as the solution rates were increased.

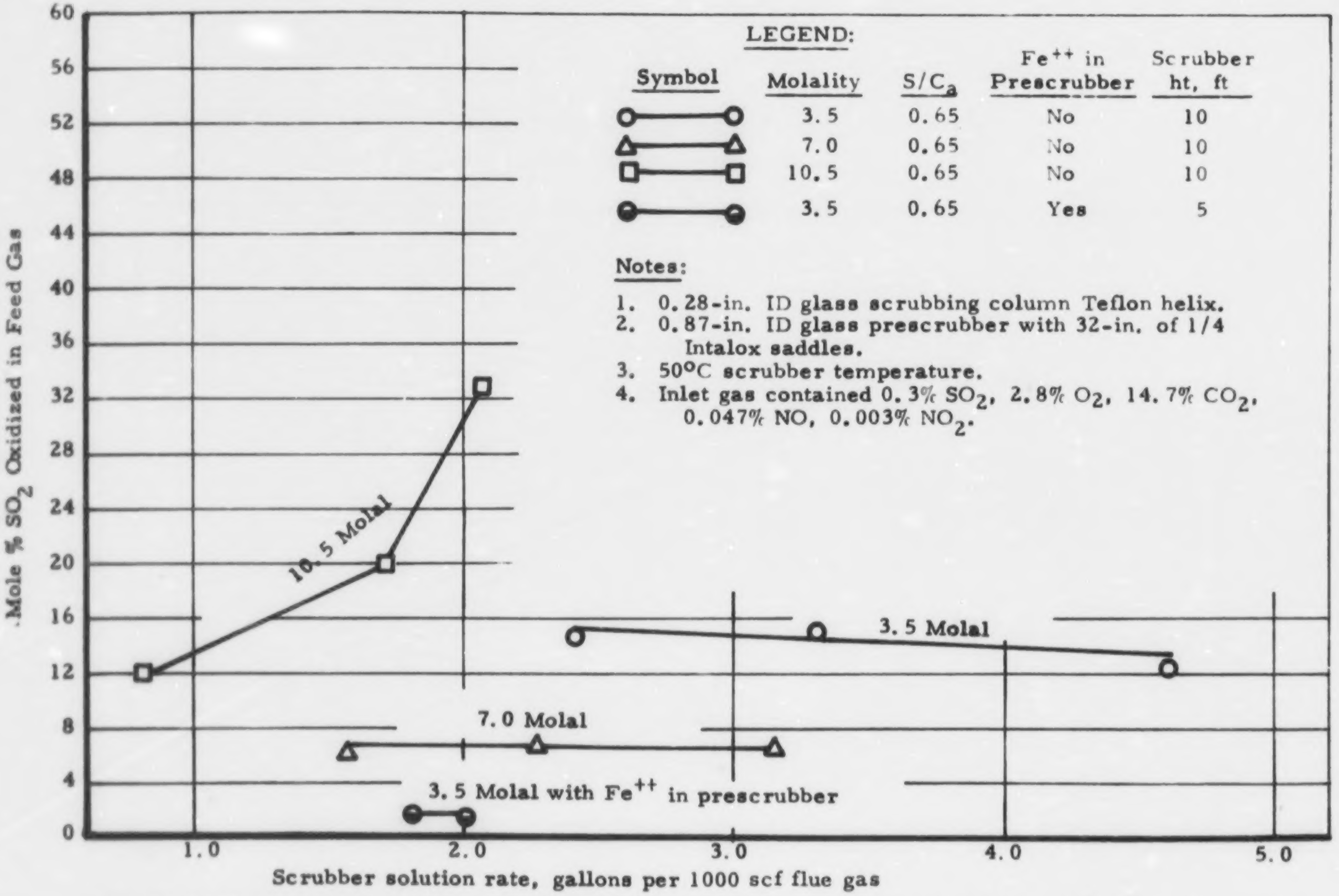


Notes:

1. 5.0 liter/min feed gas containing 0.30% SO_2.
2. Lean solution contains 1.81 moles active sodium/liter and 1.22 moles of SO_2/liter.
3. Each mole of SO_2 oxidized to $SO_4^=$ lowers the active sodium content of the rich solution by two moles.

THEORETICAL EFFECT OF SO_2 OXIDATION ON RICH S/C_a IN A ONCE THROUGH SCRUBBER

Figure 7



LEGEND:

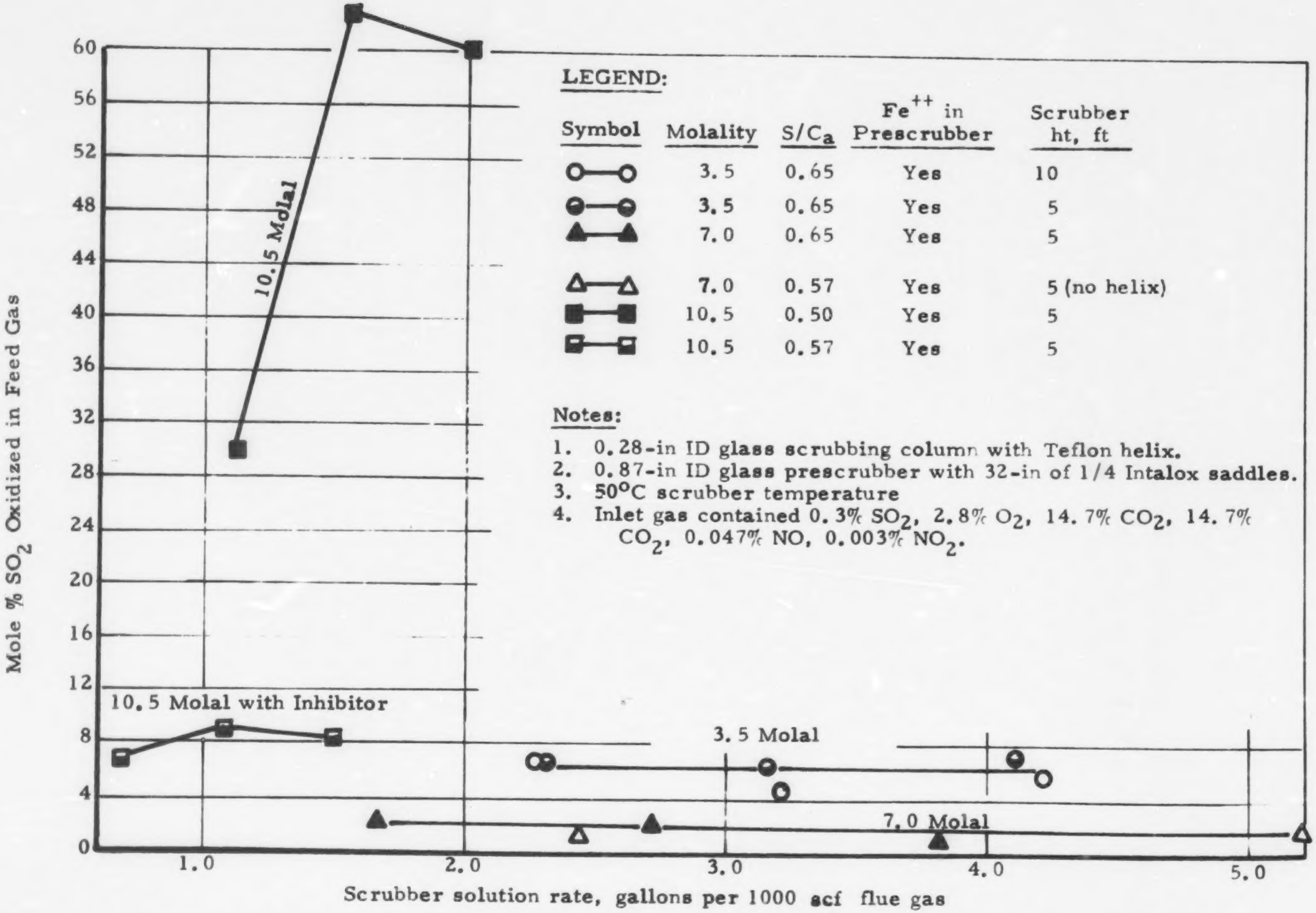
Symbol	Molality	S/C_a	Fe^{++} in Prescrubber	Scrubber ht, ft
○—○	3.5	0.65	No	10
△—△	7.0	0.65	No	10
□—□	10.5	0.65	No	10
●—●	3.5	0.65	Yes	5

Notes:

1. 0.28-in. ID glass scrubbing column Teflon helix.
2. 0.87-in. ID glass prescrubber with 32-in. of 1/4 Intalox saddles.
3. 50°C scrubber temperature.
4. Inlet gas contained 0.3% SO_2, 2.8% O_2, 14.7% CO_2, 0.047% NO, 0.003% NO_2.

OXIDATION VS SOLUTION RATE FOR SODIUM SCRUBBING SOLUTION IN ONCE THROUGH SCRUBBER

Figure 8



LEGEND:

Symbol	Molality	S/Ca	Fe^{++} in Prescrubber	Scrubber ht, ft
○—○	3.5	0.65	Yes	10
◒—◒	3.5	0.65	Yes	5
▲—▲	7.0	0.65	Yes	5
△—△	7.0	0.57	Yes	5 (no helix)
■—■	10.5	0.50	Yes	5
◩—◩	10.5	0.57	Yes	5

Notes:

1. 0.28-in ID glass scrubbing column with Teflon helix.
2. 0.87-in ID glass prescrubber with 32-in of 1/4 Intalox saddles.
3. 50°C scrubber temperature
4. Inlet gas contained 0.3% SO_2, 2.8% O_2, 14.7% CO_2, 14.7% CO_2, 0.047% NO, 0.003% NO_2.

OXIDATION VS SOLUTION RATE FOR POTASSIUM SCRUBBING SOLUTION IN ONCE THROUGH SCRUBBER

Figure 9

10. Effect of Type of Scrubber

A comparison of the amount of oxidation under similar conditions with no NO_x and a minimum of iron or fly ash shows that the oxidation in the recirculating scrubber is two to five times greater than the oxidation in the once through scrubber. Compare Runs 3, 4, 8-1, and 8-2, (Table 19) with Run 3 in Table 20. The much lower level of oxidation found in the once through scrubber is due to a lower amount of oxygen absorbed in that scrubber solution.

Similar runs, which were made with the 5-ft and 10-ft once through scrubbers (see Figure 9, ○ and ◒ points) indicate very little difference in the amount of oxidation. A similar set of runs, made with and without the helix in the column (see △ and ▲ points in Figure 9), showed only a small difference in the level of oxidation. No explanation can be offered at this time to account for these results. It would seem that the top half of the 10-ft column (where very little SO_2 is absorbed and where oxygen from the gas would be absorbed into the lean solution, which is high in sulfite) would promote high levels of oxidation. In the 5-ft column, where there is only one-half of the liquid surface area, most of the area is used in absorbing SO_2, so that the average solution sulfite concentration and pH are much lower. Inasmuch as the amounts of oxidation were found to be similar in the two cases, it must be concluded that other factors were involved. The removal of the Teflon helix from the column lowered the amount of liquid surface in the column, and also lowered the gas turbulence. This was reflected by a relatively large loss in SO_2 scrubbing efficiency. Under these circumstances it is logical to expect a large decrease in the extent of oxidation, but such was not experienced. Evidently, a better understanding of the oxidation mechanism is needed in order to be able to predict the level of oxidation.

11. Effect of NO_2 Removal in the Prescrubber

Since it was found that most of the oxidation is due to NO_2 in the scrubber, it is assumed that if the NO_2 could be removed in the prescrubber the rate of oxidation would be lowered to about the same rates as that caused by the oxygen in the flue gas. This was found to be substantially correct when an efficient prescrubber similar to that described in Appendix A, Section I, was used circulating a solution containing Fe^{++} ion.

Runs 27-1 and 27-2 (Table 19) with a feed gas containing normal amounts of NO_x and with 5.5% $FeSO_4$ in the prescrubber resulted in $< 2\%$ oxidation or about the same that would be expected with no NO_x in the feed gas. However, when the NO_2 in the feed gas was increased, the oxidation also increased to about 3.5%, indicating that not all of the NO_2 was being removed in the prescrubber.

12. Effect of Type of Solution

a. Solution Molality

In both the sodium and potassium solutions, the 7.0 molal solutions were found to result in the lowest oxidation. Also, in both the sodium and potassium systems, the 10.5 molal solutions exhibited the highest levels of oxidation (see Table 19). This is attributed to the high sulfite concentrations and the corresponding high solution pH's, both of which tend to produce high levels of oxidation. Both sodium and potassium solutions of 10.5 molality decrease in oxidation levels as the solution circulation rate is decreased, which reduces the average solution pH, and lowers the average quantity of sulfite in the scrubber. However, this does not apply to the 7.0 molal solutions, which have higher pH's and sulfite concentrations than the 3.5 molal solutions, but nevertheless produce lower oxidation rates. Evidently more complex and offsetting factors are involved.

b. Type of Solution

The sodium sulfite-bisulfite solutions seem to have slightly lower levels of oxidation than the potassium sulfite-bisulfite solutions at 3.5 molal concentration about 5% vs > 6% - see Runs 22 and 23, (Table 19).

Both 5N and 0.5 N sodium hydroxide solutions in the once through scrubber with high NO_x in the feed gas (0.04% NO + 0.04% NO_2) had only slightly lower oxidation levels than the 3.5 molal sodium sulfite-bisulfite solutions (see Runs 37-3, 36-1, and 33-1, Table 19).

Runs 7-10 (Table 20) give the oxidation data obtained on the recirculating column with sodium hydroxide solutions and calcium and magnesium hydroxide slurries. The 5 N NaOH solution with equimolar quantities of NO/NO_2 in the feed gas produced 68% oxidation in the recirculating system compared to 31% in the once through column. This is in line with the results obtained with the 3.5 molal sodium sulfite-bisulfite systems where the oxidation was found to be several times higher in the recirculating system. The oxidation level for $Ca(OH)_2$ was found to be the lowest of the three hydroxides (38%) and highest for the $Mg(OH)_2$ (96%).

D. NO_x REMOVAL DATA

Table 21 summarizes the NO_x removal data obtained during the project for various solutions and several types of apparatus. The data show some inaccuracies due to NO_x analytical problems. It is also possible that the desired NO_x composition was not always maintained exactly due to the low gas flow rates and to the problems associated with manual control of six gas streams. The NO stream, consisting of 5% NO in N_2, was especially difficult to control since it frequently fouled the rotameter and pressure regulator. This did not make much difference during most of the runs, but when making NO_x removal determinations, a small change in NO flow rate during the times when the feed and product samples were taken could cause a substantial error in the NO_x measurements.

TABLE 21

NO_x REMOVAL WITH AQUEOUS SYSTEMS

Run No.		Scrubber		Solution			Gas NO_x Content by Rotameter Reading		NO_x ppm by Gas Analysis			% NO_x Removal	
		Type	Height	Type	Conc.	Rate (ml/min)	NO ppm	NO_2 ppm	Feed to Pre-scrubber	Feed to Scrubber	Scrubber Overhead Gas	In Pre-scrubber	In Scrubber
17-4*	From Table 19	Once-through scrubber with helical packing	10.0	Na	3.5 M	2.1	470	30	520	470	430	10	8
31-4*			5.0	K	3.5 M	2.9	400	400	807	600	440	26	20
32-3			5.0	K	7.0 M	1.6	470	30	-	434	437	-	0
32-4			5.0	K	7.0 M	1.5	400	400	-	878	520	-	41
33-3			5.0	Na	3.5 M	2.0	470	30	-	530	521	-	2
34-3			5.0	Na	7.0 M	1.6	470	30	-	496	510	-	(-3)
34-4			5.0	Na	7.0 M	1.5	400	400	-	1000	598	-	40
35-2*			5.0	Na	7.0 M	1.3	400	400	880	481	498	45	(-3)
35-3			5.0	Na	7.0 M	1.4	400	400	-	704	502	-	28
36-1			10.0	NaOH	0.5 N	2.6	400	400	-	695	691	-	0
36-2			10.0	NaOH	0.5 N	3.7	400	400	-	842	730	-	13
38-1*			10.0	NaOH	5.0 N	1.3	400	400	-	856	813	-	5
38-2			10.0	NaOH	5.0 N	1.4	400	400	-	740	640	-	13
6-2	From Table 20	Recirculating scrubber with 0.5" Intalox saddle packing	2.7	Na	3.5 M	300	470	30	550	460	430	16	5
7-3				$Mg(OH)_2$	2.5 %	350	400	400	-	880	465	-	43
8-1Δ				$Mg(OH)_2$	2.5 %	350	400	400	-	786	307	-	61
8-2				$Mg(OH)_2$	2.5 %	350	470	30	-	725	692	-	5
9-2				$Ca(OH)_2$	2.5 %	300	400	400	-	877	705	-	20
9-3				$Ca(OH)_2$	2.5 %	300	470	30	-	702	653	-	7
10-1				NaOH	5 N	400	470	30	-	583	583	-	0
10-2				NaOH	5 N	400	400	400	-	827	343	-	58

NOTES:
K = potassium sulfite-bisulfite
Na = sodium sulfite/bisulfite
3.5 M, 7.0 M = moles of base per 100 moles water in feed solution
0.5 N, 5.0 N = normality of feed solution.

* Prescrubber used in these runs only
**No SO_2 in the feed to this run - for NO_x measurement without SO_2
Δ No O_2 in the feed to this run.

Nevertheless, some trends are apparent. The data indicate that about 40-60% of the NO_x was removed when equimolar quantities of NO and NO_2 were present. The amount of NO_x removal depends upon the type of solution as well as the type of scrubber used. In the recirculating scrubber, 5N NaOH and 2.5 wt-% $Mg(OH)_2$ slurry were found to remove about 50% of the equimolar NO/NO_2 whereas the 2.5 wt-% $Ca(OH)_2$ slurry was found to remove only about 20% of the equimolar NO/NO_2 (see Runs 7-3, 8-1, 9-2, and 10-2). In the once through scrubber, 20-40% of the equimolar NO/NO_2 was removed by both sodium and potassium sulfite-bisulfite solutions (see Runs 31-4, 32-4, 34-4 and 35-3). The removal of NO_x from flue gases containing a 470/30 ratio of NO/NO_2 is in the range of 0 to 10% or to about the concentration of the NO_2 in the NO_x (about 5%).

Runs 31, 32, 34 and 35 also show that the absorption of NO_x into the sulfite-bisulfite scrubbing solutions using the 5-ft once through column had no effect on SO_2 removal efficiency.

Although the results are not conclusive, it appears that adding NO_2 to flue gas to obtain an equimolar ratio of NO/NO_2 will not lower the NO_x content of the scrubbed gas significantly.

E. SULFATE REMOVAL WITH REVERSE OSMOSIS

The possibility of separating sodium sulfate from sodium sulfite-bisulfite solutions was investigated. Calculations indicated that the osmotic pressure of these solutions was in the range of 1150-1200 psi, which could be handled with available laboratory test equipment. Evaluation of the sulfite-bisulfite-sulfate system showed that the sulfate would be retained and that some of the sulfite-bisulfite would pass through a high flux membrane.

A brief experimental program was established. Two solutions were prepared. The first was equivalent to a rich, spent solution containing sodium sulfite, sodium bisulfite, and sodium sulfate. The quantity of sulfate added was equivalent to the sulfate formed by 10% oxidation of the SC_2 absorbed from a flue gas. The second solution contained sodium bisulfite and the same quantity of sodium sulfate as in Solution 1. Sodium sulfite was not added in Solution 2 in order to check the difference in permeability, if any, between sodium sulfite and bisulfite. The solutions were prepared under oxygen-free conditions using boiled distilled water. The solution compositions are given in Table 22.

The test equipment shown in Figure 10 is one of the standard systems used for R/O membrane testing and performance. The membranes used in the test were designated as CAM-38B-80, which were formulated for high flux of brackish waters. The feed solution and the product streams were purged with nitrogen to minimize oxidation during the test runs. The test results are presented in Table 23.

The data indicate that a partial separation of sodium sulfate from sodium sulfite and/or sodium bisulfite is feasible, since up to 49% of the SO_2 content of the solution permeated through the membrane while essentially all of the sodium sulfate was retained in the waste.

The economics of the system are discussed in Part Six, Section II. C.

F. OTHER SULFATE REMOVAL STUDIES

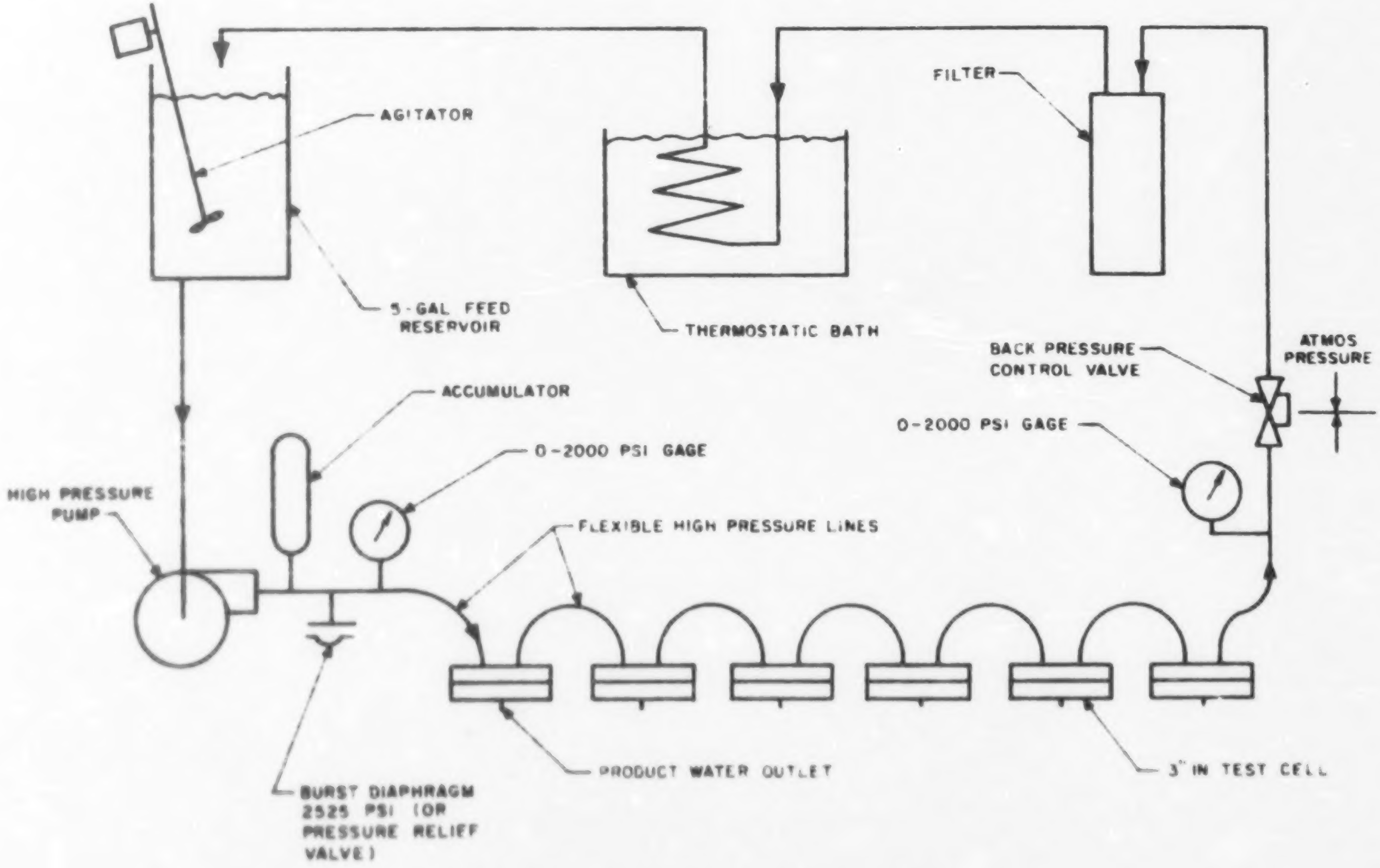
Approximate thermal requirements to regenerate zinc oxide from zinc sulfate were calculated in conjunction with the fluidized zinc oxide process (see Part Six, Section III). Although the regeneration temperature is high, this approach may have merit if oxidation of zinc sulfite to sulfate cannot be controlled at a very low level.

The investigation of the use of ion exchange methods for removal of sulfate from the sulfite-bisulfite absorbent was not pursued due to the probable high cost (again compared with the direct addition of lime as proposed in the Johnstone Zinc Oxide process). An ion exchange system would be burdened not only with the initial cost of resins, but also with resin replacement costs due to attrition, and with regenerant chemical costs.

TABLE 22

REVERSE OSMOSIS TESTS
SOLUTION COMPOSITION

Component	Sol. No. 1	Sol. No. 2
Water	3000 ml	3000 ml
$NaHSO_3$	436.8 g	606.6 g
Na_2SO_3	87.6 g	–
Na_2SO_4	17.4 g	17.4 g
Theoretical content:		
SO_2	8.85 %	10.30 %
$SO_4^=$	0.332 %	0.324 %


AGITATOR
5-GAL FEED RESERVOIR
THERMOSTATIC BATH
FILTER
BACK PRESSURE CONTROL VALVE
ATMOS PRESSURE
ACCUMULATOR
0-2000 PSI GAGE
0-2000 PSI GAGE
HIGH PRESSURE PUMP
FLEXIBLE HIGH PRESSURE LINES
BURST DIAPHRAGM 2525 PSI (OR PRESSURE RELIEF VALVE)
PRODUCT WATER OUTLET
3" IN TEST CELL

TEST CELL ASSEMBLY — FLOW DIAGRAM

Figure 10

TABLE 23

REVERSE OSMOSIS TEST RESULTS

Solution	Volume ml	Test Time min	Flux gfd *	pH	SO_2		$SO_4^{=}$	
					g/ml	% thru membrane	ppm	% thru membrane
No. 1	3335	—		5.60	.0885	—	4600	—
No. 2	3416	—		4.50	.1030	—	4500	—
No. 1 + Waste	2890	—		5.58	.0968	—	5300	—
No. 2 + Waste	2921	—		4.40	.1163	—	5100	—
Product No. 1	445	75	23.7	5.20	.0378	42.7	300	6.5
Product No. 2	495	97	20.4	4.62	.0505	49.0	300	6.7

* gfd = gal/sq ft/day

There is a direct relationship between the concentration of ions to be exchanged and the quantity of regenerant chemical required. Deionization of water is usually economical only where total dissolved solids are not greater than 500 ppm (Reference 27); ion exchange processes might be economically justifiable at substantially higher concentrations only when the product has greater value than water. In the aqueous solution processes for removing SO_2 from flue gases a substantial quantity of the sulfite in the absorbent is oxidized to sulfate. For example, in the Johnstone Zinc Oxide process it was assumed that the equivalent of 10% of the absorbed SO_2 was oxidized. This resulted in a $SO_4^=$ concentration exceeding 2.5 wt-% and a $SO_3^=$ concentration $>$ 6 wt-% in the rich absorbent.

Even if an anion resin is available which would selectively exchange the sulfate ion from the absorbent mixture, the resin would have to be regenerated with sodium hydroxide or other base. The quantity of base would be theoretically equivalent to the quantity needed for direct reaction (such as the lime addition cited above). It is evident that an ion exchange system would be more expensive than the route of lime addition.

PART SIX

PROCESS AND ECONOMIC EVALUATION

I. INTRODUCTION

The objective of this task, was to support the laboratory investigations of Tasks A through D (described in Part One herein) with preliminary process evaluations, designs and/or economic analyses to illustrate the economic feasibility of the concepts undergoing scrutiny in the laboratory. In addition to these investigations, similar evaluations and analyses would be made for aqueous processes under development by other NAPCA contractors.

The evaluations performed during this period covered work on the Johnstone Zinc Oxide Process, the Fluidized Zinc Oxide Process and on the Magnesium Base Slurry Scrubbing Process. The latter is under development by Babcock and Wilcox Company for NAPCA under Contract CPA 22-69-162 (and too, more recently, by the Chemical Construction Corporation for NAPCA under Contract CPA 70-114).

II. JOHNSTONE ZINC OXIDE PROCESS

Additional economic evaluations of the Zinc Oxide process were made to supplement the data in the Phase III study (see Volume One) based on conversion of sulfur dioxide to sulfur. A reevaluation was also made of the system in which concentrated sulfuric acid is produced but with the acid being sold at lower prices than those used in the initial analysis in Phase III. These evaluations were applied to all four plant cases*. Both 90% and 70% plant factors were used for Cases 1 to 3, which apply to power generating plants. Case 4, which applies to the smelter facility, was considered only at a 90% plant factor since it would not be subject to the load variations of power plants.

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* See Appendix B for explanation.

A. CONVERSION OF SULFUR DIOXIDE TO SULFUR

The capital and operating costs were based on data developed by Allied Chemical Corp. under NAPCA Contract PH 22-68-24. This information was submitted to Aerojet by NAPCA, and provided data about the Asarco process, which uses methane to reduce essentially oxygen-free sulfur dioxide to sulfur. The capital and operating costs submitted were for a 1400 MW power plant, and were used by Aerojet without change for Cases 1 and 2. The data were factored for Cases 3 and 4. The capital investments for complete systems, including the Asarco process, are summarized in Table 24.

The profitability was estimated at both 70% and 90% plant factors. Selling prices for sulfur were set at three levels: \$10, \$20, and \$30 per long ton. Tables 25 and 26 summarize the profitability. A loss is indicated for each case.

B. CONVERSION OF SULFUR DIOXIDE TO SULFURIC ACID

In the initial Phase III analyses, sulfuric acid prices per ton were selected at three levels: \$34 which was the current price in 1968; approximately 70% of the then current - \$23.50; and at prices required to break even. These selections were governed by the fact that similar prices were being used by others in the evaluation of other SO_2 removal processes, both aqueous and nonaqueous.

Since these prices were later considered to be optimistic, the economics of the Johnstone Zinc Oxide process were reevaluated with the sulfuric acid to be sold at \$7, \$10, and \$13 per ton. These evaluations were made for the four cases, and are summarized in Table 27, at 70% plant factor, and in Table 28, at 90% plant factor. It is apparent that the data indicate a loss for all systems evaluated.

TABLE 24[*]

CAPITAL INVESTMENT SUMMARY

JOHNSTONE'S SODIUM SCRUBBING/ZINC OXIDE PROCESS WITH CONVERSION OF SULFUR DIOXIDE TO SULFUR

	Case 1	Case 2	Case 3	Case 4
Capital Investment, Thousand $				
Process Equipment	15,085	11,925	3,346	8,785
Plume Reheat Equipment	205	205	72	46
Sulfur (Asarco Process) Equipment	2,100	2,100	700	1,900
Total Plant	17,390	14,230	4,118	10,731
Working Capital	769[1]	676[1]	51[1]	622[2]
Total Investment	18,159	14,906	4,169	11,353
Capital Requirements, $/kw	12.97	8.28	18.95	-

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* See Table 110 of Volume I for comparison

1 At 70% Plant Factor

2 At 90% Plant Factor

TABLE 25*

PROFITABILITY - ZINC OXIDE PROCESS (JOHNSTONE METHOD)
PLANTS OPERATING AT 70% PLANT FACTOR
SO_2 CONVERTED TO S (ASARCO PROCESS) -- PLUME REHEAT FROM 112° TO 200°F

	Case 1			Case 2			Case 3		
	Sulfur Price, $/Long Ton								
	10	20	30	10	20	30	10	20	30
Sales, M long tons sulfur	84.5	84.5	84.5	84.5	84.5	84.5	13.3	13.3	13.3
Sales, M $	845	1690	2535	845	1690	2535	133	266	399
Operating Cost									
Process	5082	5082	5082	4473	4473	4473	1225	1225	1225
Plume Reheat	502	502	502	502	502	502	106	106	106
Sulfur (Asarco Process)	934	934	934	934	934	934	273	273	273
Total	6518	6518	6518	5909	5909	5909	1604	1604	1604
Loss, M $/Year	5673	4828	3983	5064	4219	3374	1471	1338	1205
Loss									
$/Ton of Coal	1.60	1.36	1.12	1.42	1.19	.95	2.66	2.42	2.18
Mill/kwh	.65	.55	.46	.58	.48	.39	1.09	.99	.89
Price at Break-even, $/long ton sulfur	77			70			121		

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* See Table 112 of Volume I for Comparison

TABLE 26*

PROFITABILITY - ZINC OXIDE PROCESS (JOHNSTONE METHOD)
PLANTS OPERATING AT 90% PLANT FACTOR
SO_2 CONVERTED TO S (ASARCO PROCESS)--PLUME REHEAT FROM 122° TO 172°F

	Case 1			Case 2			Case 3**			Case 4		
	Sulfur Price, $/long ton											
	10	20	30	10	20	30	10	20	30	10	20	30
Sales, M long tons sulfur	109	109	109	109	109	109	10.5	10.5	10.5	93	93	93
Sales, M $	1090	2180	3270	1090	2180	3270	105	210	315	930	1860	2790
Operating Cost												
Process	5645	5645	5645	5036	5036	5036	1137	1137	1137	3970	3970	3970
Plume Reheat	422	422	422	422	422	422	90	90	90	50	50	50
Sulfur (Asarco Process)	1049	1049	1049	1049	1049	1049	291	291	291	938	938	938
Total	7116	7116	7116	6507	6507	6507	1518	1518	1518	4958	4958	4958
Loss, M $/Year	6026	4936	3846	5417	4327	3237	1413	1308	1203	4028	3098	2168
Loss												
$/ton of coal	1.31	1.07	.84	1.18	.94	.70	3.30	3.06	2.81	-	-	-
Mills/kwh	.54	.45	.35	.49	.39	.29	1.35	1.25	1.15	-	-	-
Price at Break-even, $/long ton sulfur	65			60			145			-		

* See Table III in Volume I for comparison

** In Case 3 Operations are 330 Days per Year at 60% Capacity

TABLE 27*

PROFITABILITY - ZINC OXIDE PROCESS (JOHNSTONE METHOD)

PLANTS OPERATING AT 70% PLANT FACTOR

SO_2 CONVERTED TO SULFURIC ACID

PLUME REHEAT FROM 122° TO 200°F

	Case 1			Case 2			Case 3		
	Sulfuric Acid Price, $/ton								
	7	10	13	7	10	13	7	10	13
Sales, M tons H_2SO_4	295	295	295	295	295	295	55.4	55.4	55.4
Sales, M $	2065	2950	3835	2065	2950	3835	388	554	720
Operating Cost, M $	7329	732	7329	6720	6720	6720	1949	1949	1949
Loss, M $/Year	5264	4379	3494	4655	3770	2885	1561	1395	1229
Loss									
$/ton of coal	1.48	1.23	.98	1.31	1.06	.81	2.82	2.52	2.22
Mills/kwh	.60	.50	.40	.53	.43	.33	1.14	1.02	.90
Price at Break-even, $/ton H_2SO_4	24.85			22.78			35.18		

* See Table 112 of Volume I for comparison

TABLE 28*

PROFITABILITY - ZINC OXIDE PROCESS (JOHNSTONE METHOD)

PLANTS OPERATING AT 90% PLANT FACTOR
SO_2 CONVERTED TO SULFURIC ACID
PLUME REHEAT FROM 122° TO 172°F

	Case 1			Case 2			Case 3			Case 4		
	Sulfuric Acid Price, \$/ton											
	7	10	13	7	10	13	7	10	13	7	10	13
Sales, M tons H_2SO_4	380	380	380	380	380	380	44	44	44	324	324	324
Sales, M \$	2660	3800	4940	2660	3800	4940	308	440	572	2268	3240	4212
Operating Cost, M \$	7992	7992	7992	7383	7383	7383	1879	1879	1879	5734	5734	5734
Loss, M \$/year	5332	4192	3052	4723	3583	2443	1571	1439	1307	3466	2494	1522
Loss												
\$/ton of coal	1.50	1.18	.86	1.33	1.01	.69	2.84	2.60	2.36	-	-	-
Mills/kwh	.61	.48	.35	.54	.41	.28	1.16	1.06	.96	-	-	-
Price at Break-even, \$/ton H_2SO_4	21.03			19.43			42.70			17.70		

* See Table 111 of Volume I for comparison

C. SULFATE REMOVAL WITH REVERSE OSMOSIS

An investigation was made to determine the feasibility of using reverse osmosis for separating sodium sulfate from sodium sulfite-bisulfite solutions as an alternate to the lime used in the Johnstone Zinc Oxide process. The data indicated that the sulfate would not permeate through the membrane, and that some of the sulfite and bisulfite would pass through the membrane (the low sulfate values in the product stream are considered to be due to post-oxidation).

An analysis of the data indicates that reverse osmosis would not be economical. Table 29 shows that most of the sulfite and bisulfite would remain with the sulfate and only 6 - 7% of the SO_2 in the solution could be separated from the sulfate. Dilution of the solution before reverse osmosis, however, would improve recovery. For example, if Solution 1 is diluted 10:1 and it is assumed that 90% of the volume can be recovered, then

33.35 liter x 8.85 g/liter = 295 g SO_2 in feed

and 30.01 liter x 3.78 g/liter = 114 g SO_2 in product

or 39% of the SO_2 would be recovered.

Similar treatment of Solution 2 indicates 44% recovery of the SO_2.

The data from Solution 1, as applied to Case 1, a 1400 MW power plant, is compared with the system using lime for removal of the sulfate in Table 30. As in the Phase III study, it was assumed that the equivalent of 10% of the SO_2 absorbed from the flue gas is oxidized. The cost data for the lime system was derived from the Phase III work. Reverse osmosis costs were based on the estimated total cost of desalinating brackish water at $1.00 per 1000 gal. product. This cost, applied to the sulfite-bisulfite-sulfate system specified, is probably optimistic.

It is apparent that removing sulfate with reverse osmosis would be substantially more expensive than the lime treatment system. The higher sulfur value loss in the R/O system would also add to the cost of sulfate removal.

TABLE 29

REVERSE OSMOSIS TEST RESULTS

	Solution	
	No. 1	No. 2
Feed - volume, ml	3335	3416
SO_2 content, g/ml	0.0885	0.1030
Total SO_2, g	295	352
$SO_4^=$, ppm	4600	4500
Product - volume, ml	445	495
SO_2 content, g/ml	0.0378	0.0505
Total SO_2, g	16.82	25.00
SO_2 recovered, %	5.7	7.1
$SO_4^=$, ppm	300	300

TABLE 30

SODIUM SULFATE REMOVAL FROM SULFITE/BISULFITE ABSORBENT

	ZnO Process - Case 1 - 1400 MW Plant	
	Using Lime for Sulfate Removal	Using R/O for Sulfate Removal
SO_2 Oxidized, lb/min	121	121
Na_2SO_4 equivalent, lb/min	268	268
$CaSO_4 \cdot 2\,H_2O$ equiv., lb/min	325	
CaO makeup, lb/min	106	
R/O Feed, 10:1 dil., gpm		6070
Sulfate, Free Recovery, gpm		2367
Waste, gpm		3703
SO_2 equiv. in waste, lb/min		180
Na_2CO_3 makeup:		
For sulfate loss, lb/min		200
For SO_2 loss in waste, lb/min		300
SO_2 Lost from Flue Gas, %	10	24.7
Operating Cost per Ton of Coal		
CaO @ $18.00/ton	$0.100	
Na_2CO_3 @ $1.60/cw		$0.827
Utilities	$0.020	
Fixed Costs	$0.045	
R/O @ $1/1000 gal product		2.370
Total Operating Cost, $/ton coal	$0.165	$3.397

III. FLUIDIZED ZINC OXIDE PROCESS

A. INITIAL APPROACH

The laboratory investigation involving the use of zinc oxide in a fluidized bed to absorb SO_2 has been discussed in Part Two. In conjunction with this study, preliminary process and economic evaluations were made to determine the economic feasibility of the system. These evaluations were made on the basis of a new 1400 MW plant and were compared with the cost estimates of the Johnstone Zinc Oxide process.

An evaluation was concerned with heat input requirements for the thermal regeneration of zinc oxide from the solid absorbent. At the time, absorption rates had not been determined. Consequently, various levels of absorption and oxidation were assumed and the heat required to regenerate the zinc oxide from zinc sulfite at $527^{\circ}F$ and from zinc sulfate at $1832^{\circ}F$ was calculated. The system is illustrated in Figure 4. The study showed that maximum conversion of zinc oxide to sulfite during absorption with minimum oxidation to sulfate was important in order to keep heat requirement costs at a minimum. Order-of-magnitude heat input requirements are listed in Table 31. A preliminary check of the heats of reaction in the absorber indicated that the heat evolved would maintain or slightly exceed the $122^{\circ}F$ absorber temperature. It was noted that heat exchange could reduce the total heat input requirements since the regenerated zinc oxide must be cooled to absorption temperature (approximately $122^{\circ}F$).

An alternate route was also considered for the removal and recovery of zinc sulfate from its mixture with zinc oxide, i.e., by leaching the soluble zinc sulfate from the mixture of zinc sulfate and insoluble zinc oxide. This system was checked for thermal requirements and there was an indication that a leaching approach to zinc sulfate removal might be a more economical system than regeneration of zinc oxide from zinc sulfate at $1832^{\circ}F$, if there was a market for zinc sulfate.

TABLE 31

HEAT INPUT REQUIREMENTS TO REGENERATE ZINC OXIDE

1400 MW POWER PLANT

Absorption %[1]	Oxidation %[2]	Regen. @ 1832°F %[3]	Theor. Heat Input, MM Btu/Min		Total
			Regen. @ 527°F	Regen. @ 1832°F	
Fluidized-bed ZnO System					
15	20	50	2.5	1.5	4.0
30	20	50	2.2	1.0	3.2
60	20	50	2.1	0.7	2.8
30	10	50	2.3	0.8	3.1
30	40	50	2.0	1.5	3.5
30	20	25	2.4	0.8	3.2
30	20	100	2.1	1.5	3.6
Johnstone Zinc Oxide Process			—	—	2.7

[1] Conversion of zinc oxide to sulfite, %

[2] Sulfite oxidized to sulfate, %

[3] Sorbent from 527°F regenerator to 1832°F regenerator, %

B. FINAL APPROACH

1. Introduction

It is expected that additional development work would determine that oxidation of the zinc sulfite to zinc sulfate would be controlled so that recovery of zinc oxide from the sulfate would be minimal. Therefore, order-of-magnitude capital and operating costs were estimated for the optimized process using fluidized zinc oxide as the absorbent for SO_2.

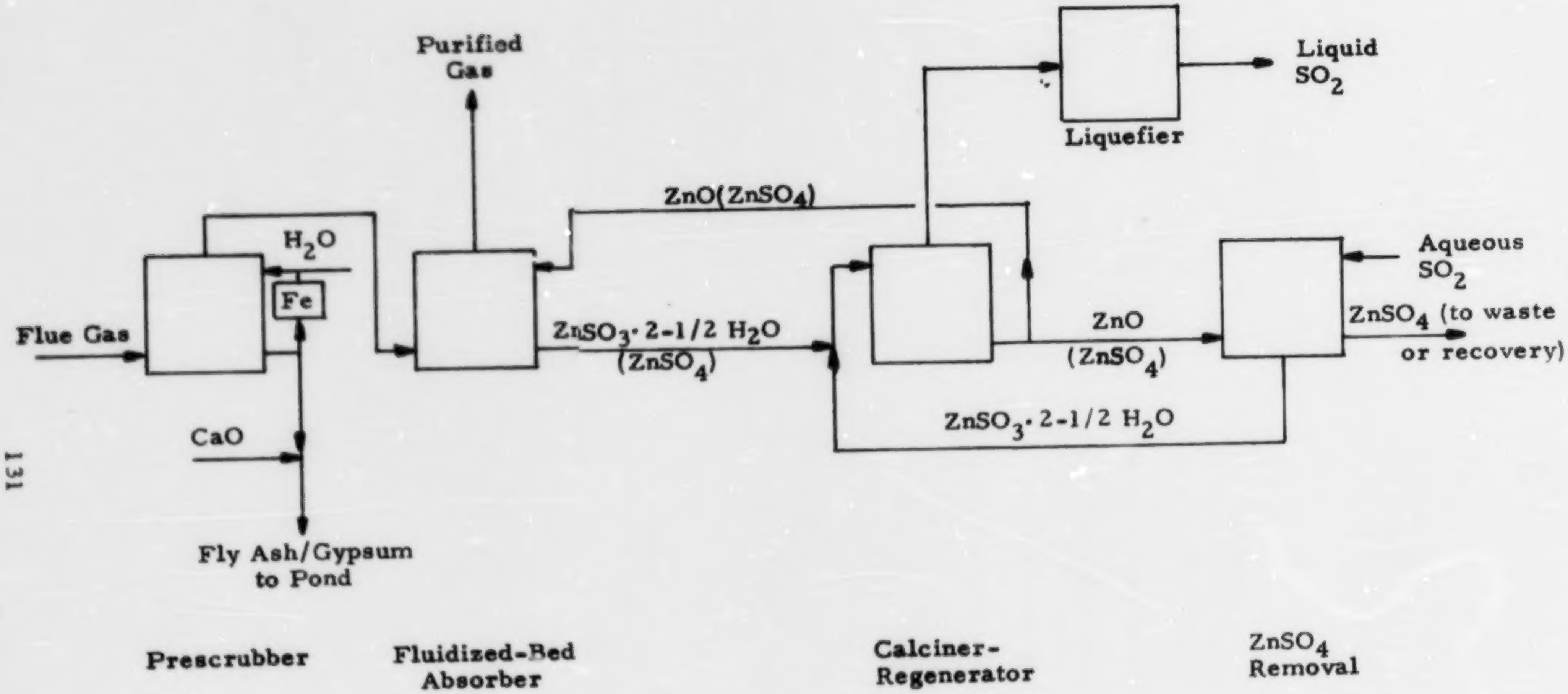
A block flow diagram of the process is shown in Figure 11. The process involves: aqueous prescrubbing of the gas to remove fly ash and NO_2; the absorption of SO_2 from the scrubbed gas by zinc oxide, thereby forming zinc sulfite; the subsequent thermal decomposition of the sulfite to re-form SO_2, which is recovered and liquefied, and zinc oxide, which is returned to the absorber; and an auxiliary system for the recovery of zinc values from process impurities, such as zinc sulfate. The conditions under which the various process steps should be carried out appear in Part Four.

The following cost estimate is based on the use of the process as applied to a new 1400 MW power plant installation. Profitability has been based on the sale of liquid SO_2, considered at various prices.

2. Capital Cost Estimate

Table 32 summarizes the capital costs. The prescrubber system selected is a two-stage mobile bed scrubber with a collection efficiency in excess of 99% for particles of 2 microns and larger when 5 gallons of water is circulated per 1000 cubic feet of gas (Reference 28). Additional design and cost data were obtained from a recent TVA study (Reference 29). The prescrubber system includes the scrubbers, piping, pumps, foundations and supports, and hold tank.

A recent report by Tracor, Inc. was used as a guide for the design and cost estimating of fluidized bed systems (Reference 30). The


Purified Gas
Liquid SO_2
Liquefier
$ZnO(ZnSO_4)$
H_2O
Fe
Flue Gas
$ZnSO_3 \cdot 2\text{-}1/2\ H_2O$
$(ZnSO_4)$
ZnO
$(ZnSO_4)$
Aqueous SO_2
$ZnSO_4$ (to waste or recovery)
$ZnSO_3 \cdot 2\text{-}1/2\ H_2O$
CaO
Fly Ash/Gypsum to Pond
Prescrubber
Fluidized-Bed Absorber
Calciner-Regenerator
$ZnSO_4$ Removal

BLOCK DIAGRAM - OPTIMIZED FLUIDIZED ZINC OXIDE PROCESS

Figure 11

TABLE 32

FLUIDIZED ZINC OXIDE PROCESS - CAPITAL COST ESTIMATE

(1400 Megawatt New Power Plant)

	Investment, $
Prescrubber System	1,600,000
Fluidized Bed Absorption System	1,320,000
Absorption System Mechanical Separator	1,110,000
Prescrubber/Absorption System Fan (For 13.5" $H_2O \Delta P$)	940,000
Fluidized Bed Regeneration System	550,000
Regeneration System Mechanical Separator	70,000
Regeneration System Fan	110,000
Conveyors	160,000
Waste Disposal System	90,000
Zinc Sulfite Recovery System	150,000
Sub-total	6,100,000
Sulfur Dioxide Liquefaction System	600,000
Total Fixed Capital	6,700,000
Working Capital	670,000
Total Investment	7,370,000

equipment of interest included the absorption system, with cyclonic mechanical separator, and the regeneration system, with cyclonic mechanical separator and fan. The purchased equipment cost was based on Tracor data relating to their fluidized copper oxide process, with the cost recalculated to conform with the lower gas and solid flow rates and lower operating temperatures that will be used in the fluidized zinc oxide process. The purchased equipment cost was subsequently factored to obtain the fixed capital cost.

The absorption system fan cost was based on $50,000 per inch of water pressure drop for 1000 MW plants, and factored to 1400 MW. Conveyor costs were based on available data used in previous estimates.

The waste disposal system cost was factored from costs shown in Reference 29 for 10% slurry systems pumped to a pond, and with no water recirculation from the pond.

The recovery system equipment costs include a gasifier, filter, mixer-crystallizer, and centrifuge, at a level capable of handling the 5% sidestream of the solid absorbent mixture that would be needed if oxidation occurred to the extent of 0.5%.

The SO_2 liquefaction plant cost was factored from costs reported in a Bureau of Mines report (Reference 36). Although the scale-up from the reference estimate to a 1400 MW plant is considerable, the capital cost indicated is believed to be adequate for the liquefaction of all of the recovered sulfur dioxide.

Plume reheat equipment was not included in the cost estimates, inasmuch as the purified gas temperature should approach 155°F (due to the heat of reaction), which may be adequate for most locations.

The estimated total fixed capital cost of $6, 700, 000 is substantially lower than costs appearing in the literature for other regenerative SO_2 removal processes. This is attributed to:

- Simplicity of the fluidized zinc oxide process, which requires only three major unit operations as a result of the non-occurrence of interfering secondary reactions.
- Low operating temperatures.
- High SO_2 sorption capacity of zinc oxide which reduces equipment size.

3. Operating Cost Estimate

Operating costs were derived from the schedule shown in Table 33, indicating a cost of $0.64/ton coal and 0.26 mill/kwh. Raw material and chemical costs are listed in Table 34. Sixteen operators would be required for continuous operation, or four men per shift. A wage rate of $4.00 per man-hour was used. Utilities costs are detailed in Table 35. It is assumed that suitable steam would be available at the power plant for regeneration of the spent absorbent. The waste disposal costs are based on a 10% fly ash slurry being routed to a pond on the plant site at a cost of $0.70 per dry ton. The other operating cost elements are self-explanatory.

Although Aerojet is aware that NAPCA has standardized on a 70% plant factor, a 90% plant factor (330 days operation) was used in this estimate in order to provide a level of operation that would be comparable with that used in most cost estimates appearing in the literature. Under this conditions the process appears to be technically and economically superior to many other regenerative SO_2 removal processes.

TABLE 33

FLUIDIZED ZINC OXIDE PROCESS
OPERATING COST ESTIMATE

(1400 Megawatt New Power Plant, 90% Plant Factor)
Fixed Capital Investment: $6, 700, 000

	ITEM	TOTAL $	%
1.	Raw Materials and Chemicals	346,600	11.8
2.	Direct Labor	128,000	4.4
3.	Supervision, 15% of 2.	19,200	0.7
4.	Maintenance, 3% of fixed capital cost	201,000	6.8
5.	Supplies, 20% of 4.	40,200	1.4
6.	Utilities	1,034,500	35.2
7.	TOTAL DIRECT COST	1,769,500	60.3
8.	Payroll Burden, 18.5% of 2 & 3	27,200	1.0
9.	Plant Overhead, 50% of 2, 3, 4 & 5	194,200	6.6
10.	Waste Disposal	6,700	0.2
11.	TOTAL INDIRECT COST	228,100	7.8
12.	Depreciation, 11% fixed capital cost	737,000	25.1
13.	Taxes & Insurance, 3% fixed capital cost	201,000	6.8
14.	TOTAL FIXED COST	938,000	31.9
15.	TOTAL OPERATING COST	2,935,600	100.0

16. Cost: $0.64/ton coal, 0.26 mill/kwh

TABLE 34

FLUIDIZED ZINC OXIDE PROCESS - RAW MATERIALS AND CHEMICALS

(1400 Megawatt New Power Plant, 90% Plant Factor)

	Cost per year, $
ZnO[a], 2,297,000 lb @ $0.15/lb	344,500
50% NaOH[b], 72,000 lb @ $2.90/cw	2,100
Total	346,600

---

[a] Make-up based on loss of 0.2% of solids circulated to the regenerator.

[b] Requirement for recovering zinc values from impurities, including sulfate, equivalent to 0.5% oxidation of the SO_2 absorbed. Na_2SO_4 formed is discarded.

TABLE 35

FLUIDIZED ZINC OXIDE PROCESS - UTILITIES
(1400 Megawatt New Power Plant, 90% Plant Factor)

	Cost per year, $
Steam, 1,350,000,000 lb @ $0.50/1000 lb	675,000
Power, 48,660,000 kwh @ $.006/kwh	292,000
Process Water, 415,000,000 gal @ $.10/1000 gal	41,500
Cooling Water, 520,000,000 gal @ $.05/1000 gal	26,000
Total	1,034,500

4. Profitability

The profitability of any SO_2 removal system that produces a salable product is obviously dependent upon the market conditions relating to the product. The ultimate demand for elemental sulfur, SO_2, and H_2SO_4 as products is controlled by the demand for sulfuric acid, inasmuch as both elemental sulfur and SO_2 would eventually be converted to the acid to a large extent. Over 70% of the sulfuric acid produced in the United States is derived from native sulfur. A large new source for sulfur, or SO_2, such as the sulfur values contained in flue gases, would result in a continued drop in sulfur prices. Sulfuric acid (100%) sold for $33.75 per ton in July 1969, which is equivalent to $12.34 per long ton of sulfur value (Reference 31). World-wide sulfur prices in recent months have been fluctuating between $22.50 and $45.50 per long ton (References 32 and 33). The list price in January 1970 was $39 to $40 per long ton, with prices eroding as much as $15 per long ton as a result of large world inventories (Reference 34).

The profitability of the fluidized zinc oxide process is presented in Table 36 with SO_2 prices based on four levels of sulfur prices, as follows:

Sulfur $/long ton	Sulfur Dioxide Equivalent $/short ton
10	4.50
20	9.00
30	13.50
39	17.50

According to the present day market, it would be expected that SO_2 could sell for between $9.00 and $13.50 per ton, plus some additional revenue due to value added above the elemental sulfur value. A break-even situation would be expected for the fluidized zinc oxide process with SO_2 sales at $10.87 per ton. Even at $4.50 per ton of SO_2, the cost per ton of coal is not excessive.

This economic study of the fluidized zinc oxide process, though quite preliminary, indicates that it should be superior to many other regenerable processes for the removal of SO_2 from flue gases.

TABLE 36

FLUIDIZED ZINC OXIDE PROCESS: PROFITABILITY

(1400 Megawatt New Power Plant)
90% Load Factor

Total Investment: $7,370,000
Liquid SO_2 Sales: 270,000 tons/year (95% recovery)

	Liquid SO_2 Price, $/ton			
	4.50	9.00	13.50	17.50
Sales, M $	1215	2430	3645	4725
Operating Cost, M $	2936	2936	2936	2936
Profit (loss), M $	(1721)	(506)	709	1789
Profit After Tax, M $	-	-	369	930
Return on Investment After Tax, %	-	-	5.0	12.6
Payout, Years	-	-	6.7	4.4
Net Profit (Cost)*				
$/ton of coal	(0.37)	(0.12)	0.08	0.20
mills/kwh	(0.16)	(0.05)	0.03	0.08

---

* Operations would break-even if SO_2 was sold at $10.87/ton.

IV. MAGNESIUM BASE SLURRY SO_2 SCRUBBING SYSTEM

A. INTRODUCTION

The Research and Development Division, Babcock and Wilcox Company, performed development work for NAPCA under Contract CPA 22-69-162 entitled: "Magnesium Base Slurry Scrubbing of Pulverized Coal Flue Gas."

The work was involved with: (1) the design and construction of a pilot plant scrubbing system having a nominal capacity of 1000 scfm flue gas, and (2) with experimental work concerning the removal of fly ash and sulfur dioxide from flue gas generated by burning pulverized coal. Regeneration of the absorbent was not included in the scope of the project.

One of Aerojet's tasks in Phase IV of Contract No. PH 86-68-77 was to provide economic evaluation of aqueous processes under development for NAPCA such as the above-mentioned Babcock & Wilcox process. Unfortunately, the schedule of the B&W contract precluded analysis of this system during the early months of the Aerojet contract. However, initial operating data were presented in B&W's progress report for the month of January 1970, making it possible to start a cost analysis. Several runs appeared in this report in which a venturi scrubber was used as the prescrubber to trap fly ash, and a floating bed absorber was used to remove the SO_2 from the flue gas. Run D-047 of the series of runs was selected as a guide for the Aerojet cost analysis; this was an arbitrary choice from several runs that had removed $> 95\%$ of the SO_2 present in the flue gas.

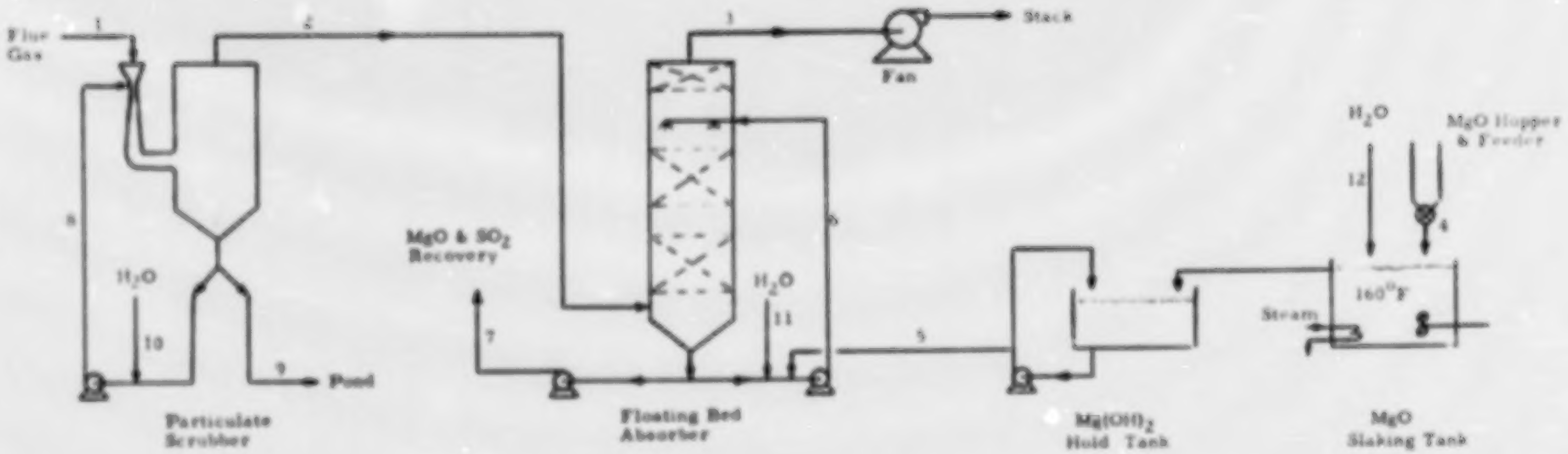
B. PROCESS ENGINEERING

Most of the data of Run D-047 were converted directly to a 1400 MW power plant size by a factor derived from the ratio of gas flow in the pilot plant to the gas flow in a 1400 MW plant (Cases 1 and 2 of the Aerojet Phase III study). The venturi scrubber product fly ash concentration was increased from a very dilute to a 10% slurry in order to economize on water consumption. Temperatures and gas pressures were not changed.

Figure 12 illustrates a simplified flow diagram of the magnesium base slurry SO_2 scrubbing system (similar to the B&W pilot plant design) with pertinent operating data for a 1400 MW system. Material quantities shown are approximate and do not balance since they were calculated from Run D-047 stream data and are not necessarily theoretical quantities. No attempt was made to determine the exact composition of the circulating slurry to the floating bed absorber, since this was not needed for the cost estimates. It was assumed that the floating bed absorber product liquor would flow to an absorbent regeneration and SO_2 recovery system. No data were given on this system; consequently, the system is not included in this preliminary study.

Design and cost information is limited concerning venturi scrubbers with adequate capacity to handle the large quantities of flue gas generated in large power plants. Data in a recent report (Reference 35) indicated that four 12-ft dia. x 20-ft high venturi prescrubbers would be needed for a 300 MW system handling 671,600 acfm gas. On this basis, seventeen 12-ft dia. units would be needed for a 1400 MW plant. The report (Reference 35) did not provide cost information on these scrubbers; therefore, floating bed scrubbers were substituted to serve as prescrubbers in the cost estimate discussed below.

Run D-047 indicated a liquid/gas ratio of 18.5 gal/mcf flue gas for the floating bed absorber. At this rate approximately 55,000 gpm of circulating liquor would be needed for the SO_2 floating bed absorbers in a 1400 MW plant. Scale-up of the pilot plant floating bed absorber indicated a total area of about 3900 sq ft of absorber cross-sectional area would be needed for SO_2 removal from a 1400 MW plant. Presumably, this could be provided by installing six 29-ft dia. absorbers in parallel. It was assumed that an equivalent area would also be needed for the floating bed prescrubbers used for fly ash removal. These areas, converted to equivalent units, are similar to those used in a lime-stone-wet scrubbing study by TVA (Reference 29).


Flue Gas
1
2
3
Stack
Fan
8
H$_2$O
10
9
Pond
Particulate Scrubber
MgO & SO$_2$ Recovery
7
Floating Bed Absorber
H$_2$O
11
6
5
Mg(OH)$_2$ Hold Tank
H$_2$O
12
MgO Hopper & Feeder
4
160°F
Steam
MgO Slaking Tank

DESCRIPTION	STREAM NO. 1	2	3	4	5	6	7	8	9	10	11	12
Components, lb/min												
Total Gas	197000	209805	208605									
Dry Gas	188335	188335	188272									
H_2O	8665	21470	20333		11790	456200	22000	331100	3900	16700	11120	11750
SO_2	1270	1270	63									
Fly Ash	396	6	6					1090	390			
MgO				928	928							
$MgSO_3$, Solid						*	2735					
$MgSO_4$						*	94					
H_2O, gpm					1408	54700	2637	39700	467	2002	1333	1408
Temperature, °F	575	145	134	72	94	138	138	140	140	60	60	60
Gas Pressure, in. W.C.	5.4	-12.2	-25.7									

*Also in circulating slurry.

MAGNESIUM BASE SLURRY SO_2 SCRUBBING SYSTEM FOR 1400 MW POWER PLANT

Figure 12

C. CAPITAL COST ESTIMATE

Cost data on venturi scrubbers were not available; thus floating bed scrubbers were substituted for cost estimating purposes. Since the process was in an early stage of development, only an order-of-magnitude estimate could be made at this time. Even this provided only a partial cost since the system did not include regeneration of absorbent and recovery of SO_2.

Under these circumstances, cost information appearing in the TVA Report (Reference 29) was used as a guide to estimate capital costs. Table 37 provides a summary of the capital costs, with the total fixed capital estimated at $9, 750, 000. It is possible that the cost would be somewhat less if large venturi prescrubbers could be substituted.

D. OPERATING COST AND ECONOMIC ANALYSIS

Operating costs and an economic evaluation cannot be made since the process as described is incomplete. The magnesium oxide regeneration and SO_2 recovery systems will add to both the capital and operating costs. Credits applied due to reduction in magnesium oxide make-up requirements and to sale of sulfur values, however, will help to balance the added costs.

TABLE 37

MAGNESIUM BASE SLURRY PROCESS: CAPITAL COST ESTIMATE SUMMARY

(Regeneration System Not Included)

CASE 1

Item	Cost - $
MgO Storage and Handling Facilities	480,000
Slurry Storage and Pumping	150,000
Floating Bed Prescrubbing System	2,000,000
Floating Bed Absorption System	2,000,000
Solids Disposal System and Pond	90,000
Fan, 30 in. W.C. Δp	1,800,000
Control Room and Equipment	290,000
Electrical and Water Distribution	360,000
Painting and Insulation	140,000
Construction Facilities	300,000
Total Direct Cost	7,810,000
Engineering Design	470,000
Contractor's Fees and Overhead	950,000
Contingency	520,000
Total Fixed Capital Cost	9,750,000

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APPENDIX A

OXIDATION AND NO_x STUDIES

I. DESCRIPTION OF EQUIPMENT

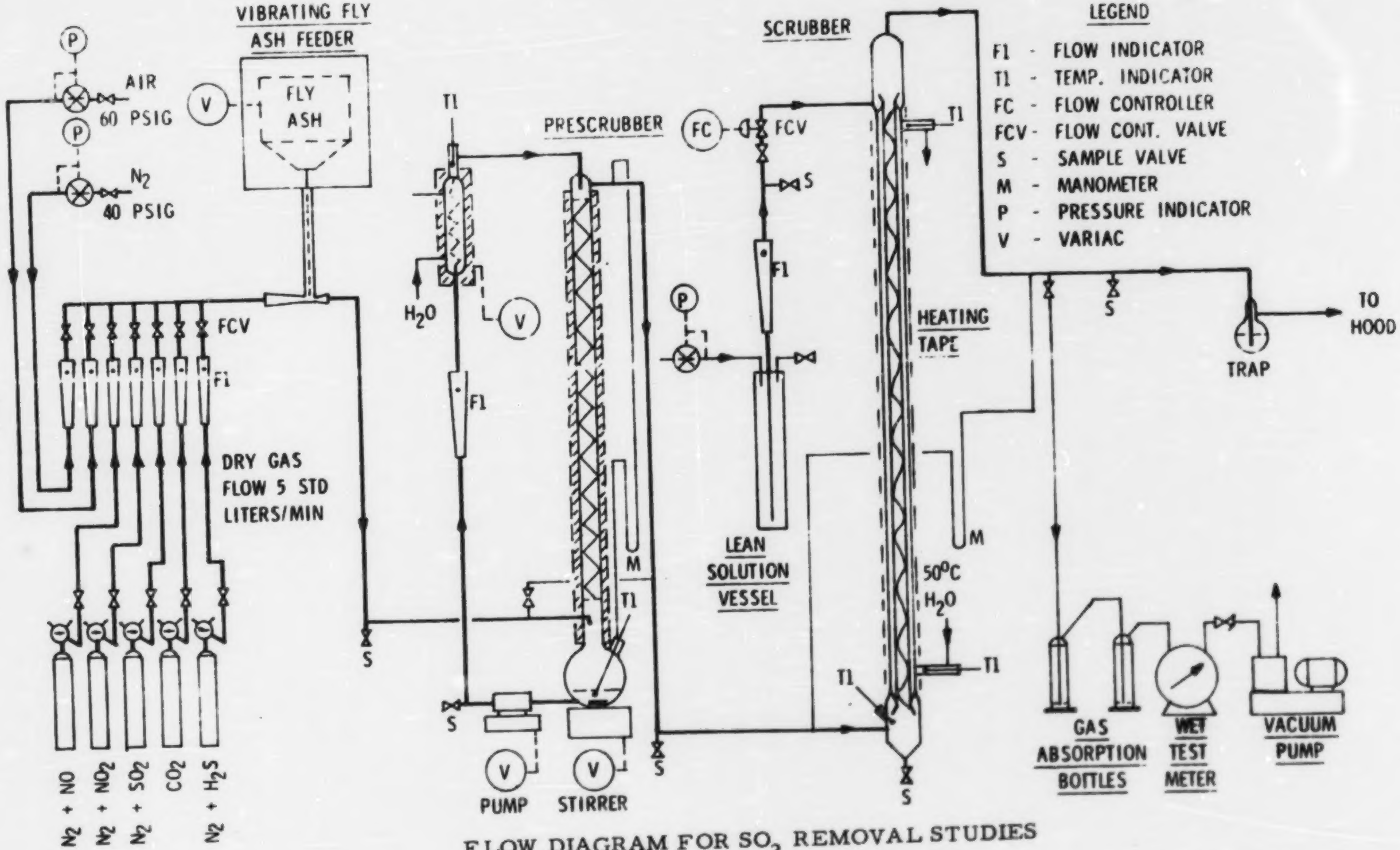
The arrangement of equipment used in these studies is shown in the flow diagram, Figure A-1.

The equipment was designed as a dynamic bench scale countercurrent prescrubber and scrubber, to simulate the SO_2 removal efficiencies of a full sized commercial plant treating flue gas from a coal burning boiler. In doing this it was hoped to obtain oxidation values of SO_2 to SO_3 in the scrubbers that are similar to oxidation that occurs in a full size plant. The equipment was made of glass and plastic to eliminate the possible catalytic effect of iron and other metals on the system. The equipment was versatile in that the SO_2, CO_2, NO, NO_2, O_2, N_2, and fly ash concentrations in the synthetic flue gas could be changed within the desirable limits simply by turning valves or switches.

The flue gas mixtures were made up of gases from the various lines and cylinders. Each gas stream was reduced to a constant pressure of 260 mm Hg (gage) by a pressure reducing regulator, metered accurately with a calibrated rotameter, and controlled with a needle valve. The gas streams consisted of:

- 4.8% SO_2 in N_2
- 5.0% NO in N_2
- 1.2% NO_2 in N_2
- Pure CO_2
- Air
- Pure N_2

It was planned to add fly ash from a vibrating hopper at a controlled rate through a sharp orifice and into a venturi mounted in the dry, mixed flue gas line. This system required revisions that are discussed later.


VIBRATING FLY ASH FEEDER
FLY ASH
V
P
AIR
60 PSIG
P
N_2
40 PSIG
FCV
FI
DRY GAS FLOW 5 STD LITERS/MIN
N_2 + NO
N_2 + NO_2
N_2 + SO_2
CO_2
N_2 + H_2S
S
TI
H_2O
V
FI
S
PUMP
V
PRESCRUBBER
M
TI
STIRRER
V
S
FC
FCV
S
FI
P
LEAN SOLUTION VESSEL
SCRUBBER
TI
HEATING TAPE
50°C H_2O
TI
TI
M
S
LEGEND
FI - FLOW INDICATOR
TI - TEMP. INDICATOR
FC - FLOW CONTROLLER
FCV - FLOW CONT. VALVE
S - SAMPLE VALVE
M - MANOMETER
P - PRESSURE INDICATOR
V - VARIAC
S
TRAP
TO HOOD
GAS ABSORPTION BOTTLES
WET TEST METER
VACUUM PUMP

FLOW DIAGRAM FOR SO_2 REMOVAL STUDIES
USING ONCE THROUGH SCRUBBER

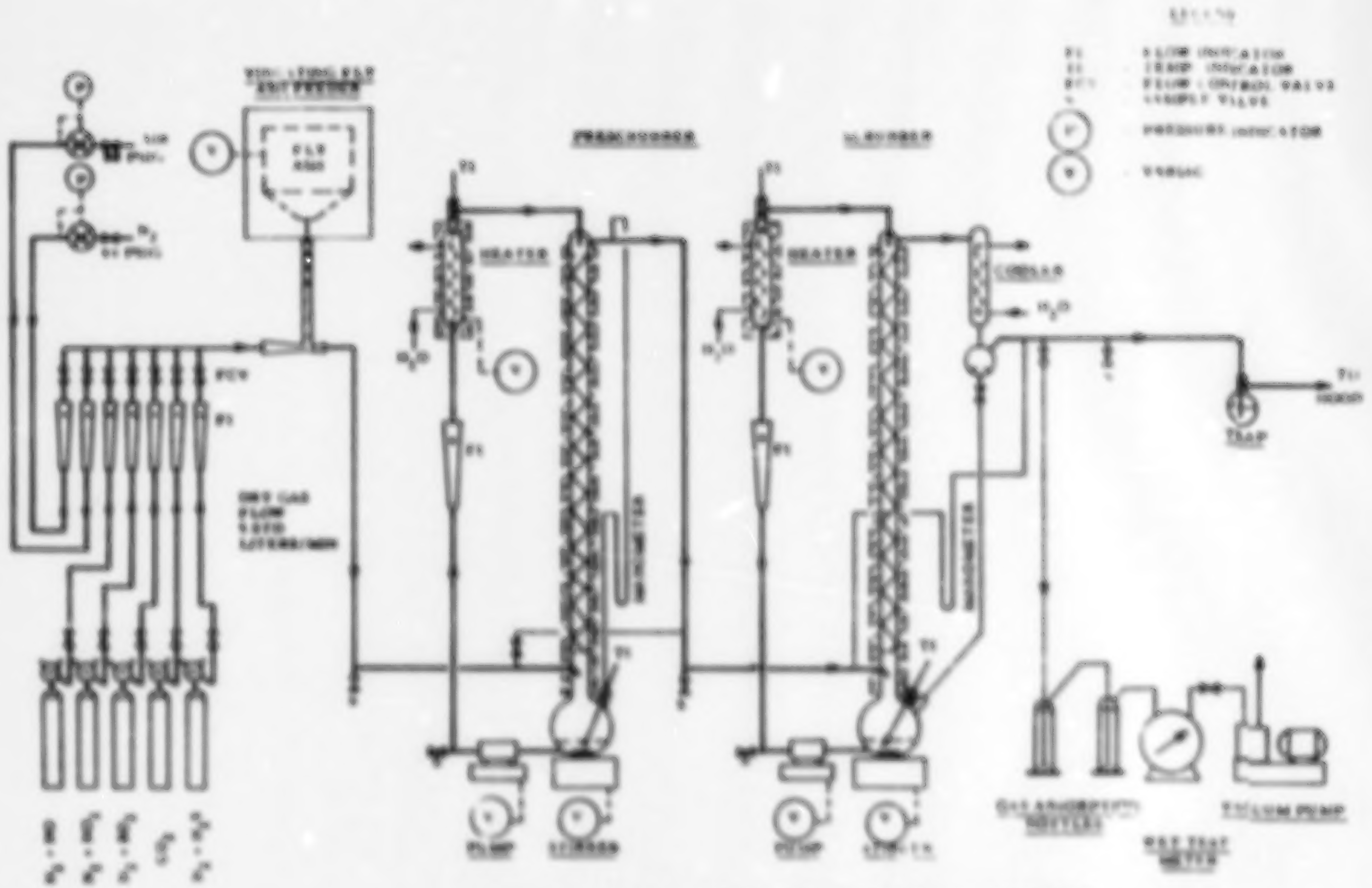
Figure A-1

The prescrubber consisted of a 22 mm ID (0.87 in.) glass column packed with 32 in. of 0.5-in. Intalox saddles. This packing was used so that slurries containing fly ash could be circulated without plugging. During some runs late in the program the 0.5-in. packing was replaced with 0.25-in. saddles in order to obtain more efficient scrubbing. A calibrated glass rotameter was used to measure the rate of liquid flow. An adjustable transformer - controlled electric heater was installed in the liquid line in order to maintain the prescrubber overhead temperature at about 50°C. The column was insulated to minimize heat losses and a stirrer was provided in the liquid receiver to prevent the solid fly ash from settling out prematurely. Thermometers were provided for inlet and outlet liquid temperature measurement. A manometer was used to measure the pressure drop across the column. Sample connections were provided for liquid and gas analyses. A small rotameter was added to provide make-up water for that carried out by the saturated warm outlet gas.

An alternate prescrubber was also used in some runs to check fly ash and removal efficiency. This system simulated a venturi scrubber by using a laboratory aspirator through which the 50°C prescrubber solution was circulated. The synthetic flue gas stream containing the fly ash flowed into a small glass gas-liquid separator. The gas stream then flowed into the scrubber.

In a few runs the dry gas mixture by-passed the prescrubber, and the water needed to saturate the gas at 122°F was metered into the preheated line.

A liquid recirculating scrubber was used initially that consisted of a packed column of the same diameter and height as the prescrubber and was packed with 0.5 in. porcelain Intalox saddles (see Figure A-2). The solution pump, rotameter, liquid heater, manometer, column insulation, thermometer, receiver stirrer and sample connections were similar to the prescrubber equipment. An auxiliary electrical heater was installed on the outside of the column and covered with insulation to compensate for heat losses and to provide a constant temperature throughout the scrubber. An electrical heater on the gas line from the prescrubber to the scrubber prevented the gas from cooling and condensing water in this line.


PRESCRUBBER
SCRUBBER
HEATER
HEATER
COOLER
H_2O
H_2O
H_2O
FCV
FI
FI
FI
TI
TI
MANOMETER
MANOMETER
TRAP
GAS ABSORPTION BOTTLES
WET TEST METER
VACUUM PUMP

FLOW DIAGRAM FOR SO_2 REMOVAL STUDIES USING RECIRCULATING SCRUBBER

Figure A-2

Another scrubber in which fresh absorbent was fed to the top and spent absorbent removed at the bottom was used in most of the tests (Figure A-1). This unit was designated as the "once through scrubber" in order to distinguish it from the recirculating scrubber. This scrubber was installed so that data could be obtained on a countercurrent operation similar to the full-sized commercial column proposed in the Johnstone Zinc Oxide Process. This type of operation had substantially different operating characteristics than the recirculating scrubber.

The original once through scrubber, which was used for the preliminary base line runs, was made from a 5 mm ID glass tube, 10-ft. long. The once through scrubber used in most of the oxidation experiments was made of 7 mm ID glass tubing, 10 ft. long. A third unit was also 7 mm ID, but only 5 ft. long. The 7 mm ID glass tube was contained in a 15 mm ID glass tube which provided a jacket through which water was circulated in order to maintain the desired 50° operating temperature. The 7 mm ID glass tubing was flared out at each end in order to permit the liquid to enter the top and leave the bottom without causing flooding. It was found necessary to add a helix of 0.033-in. thick Teflon inside of the 7 mm tubing to provide good liquid-gas contact. The lean solution was fed to the top of the column from a large reservoir by nitrogen pressure. A calibrated rotameter was used to measure the solution rate which was controlled by a Foxboro flow controller. The rich solution was collected at the bottom of the column in a small receiver from which it was withdrawn, measured and analyzed. Thermometers indicated the liquid and gas temperatures, and a manometer measured the gas pressure drop across the column.

The scrubbed gas from either of the two scrubbers passed through a water bubbler and was vented to a hood. Two sample connections were provided in the line to the bubbler. The first connection went to a gas absorption bottle, a wet test meter and a vacuum pump. The vacuum pump was necessary to draw the gas sample through the bubbler in that the pressure in the absorption system was not appreciably above atmospheric pressure. The second sample connection was used to take gas samples in glass bulbs for NO_x analysis.

Figure A-3 is a sketch of the final design of the fly ash addition unit, which had the capability to deliver a continuous fly ash stream at a rate of about 15 mg/min to the 5 liter/min to the 5 liter/min flue gas stream. It was found necessary to dilute the fly ash with a relatively large volume (99%+) of inert free-flowing glass beads (-60 + 100 mesh from the 3M Co.) in order to maintain a steady flow of fly ash. An aspirator in the dry gas line helped to control the pressure drop across the vibrating hopper-orifice feed system. The hopper discharge line was connected to the side inlet line of the aspirator. The aspirator also served to mix the fly ash-glass bead mixture with the high velocity gas stream. A needle valve in the gas line to the top of the hopper was adjusted to control the pressure drop across the fly ash orifice. The glass beads in the circulating prescrubber liquid were removed from the system in a settling bulb placed upstream of the circulating pump.

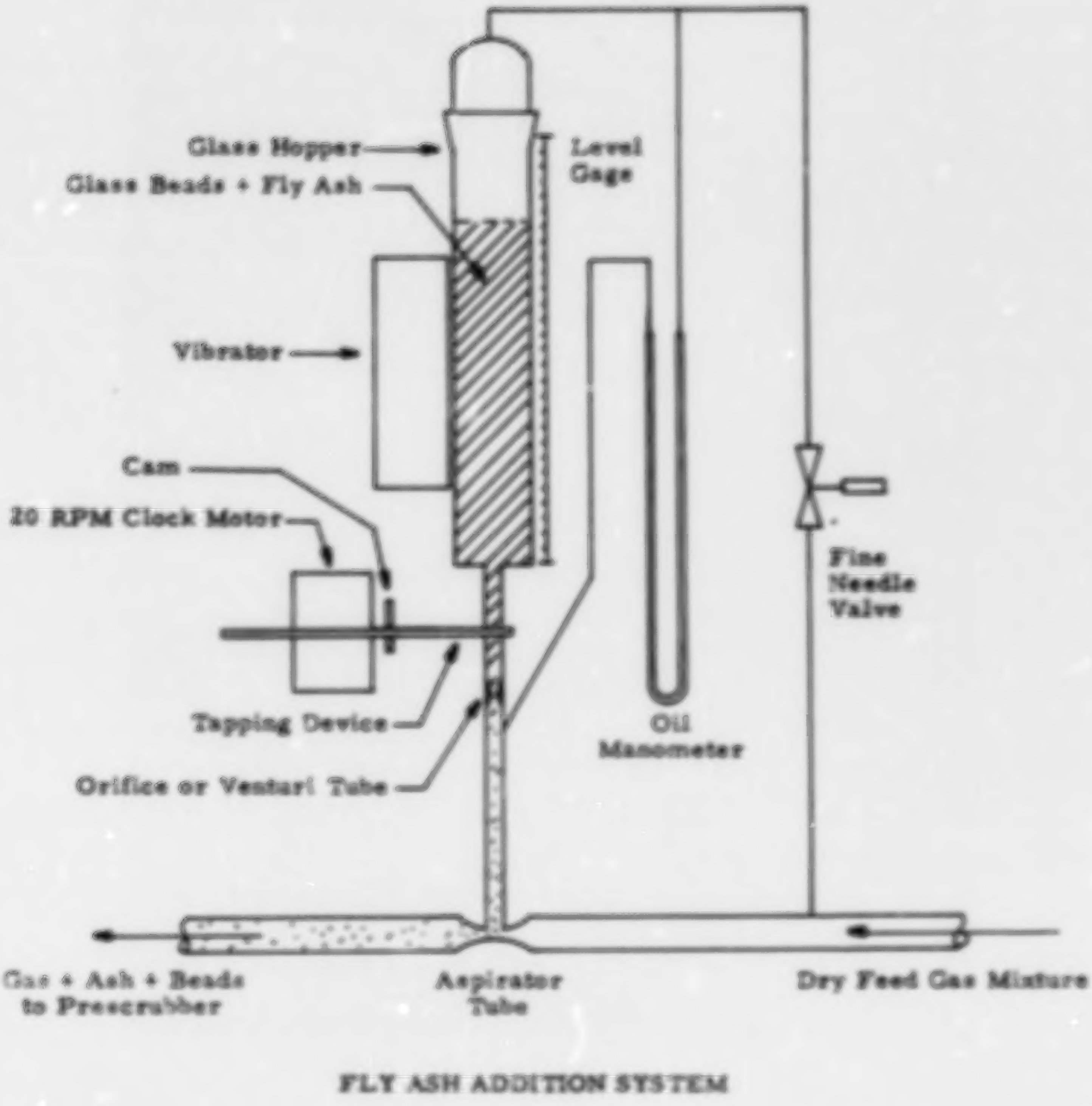
Figure A-4 is a photograph of the apparatus and work area. The once through scrubbing column is not visible, but was located at the extreme left in the picture.

II. OPERATING PROCEDURE

A. FEED GAS SYSTEM

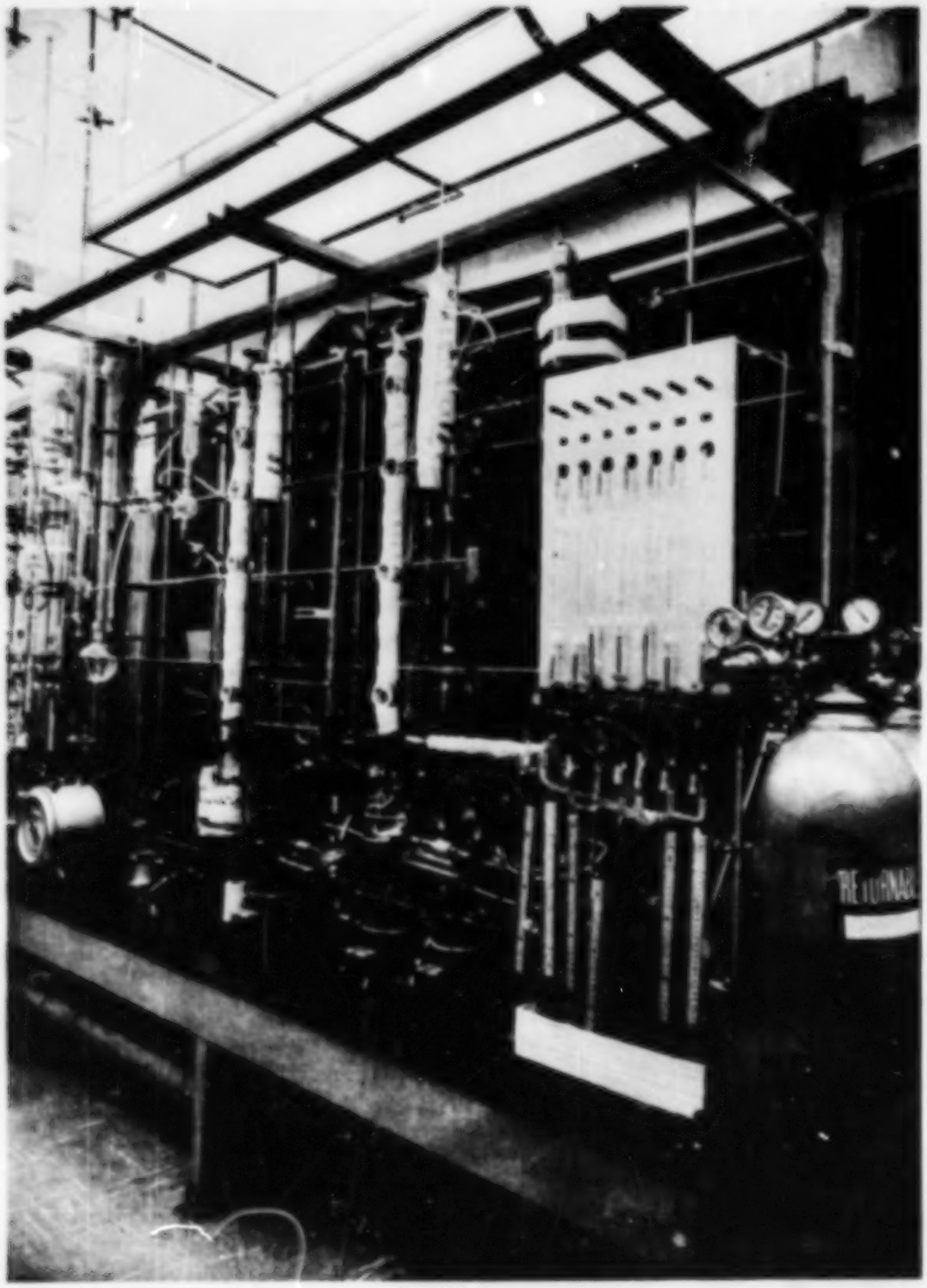
The following operating procedure was used in the experimental work performed in the bench scale equipment:

The total gas flow was held constant at a rate of 5.0 liter/min of wet (7.25% H_2O) gas flowing at 70°F and 760 mm Hg. This is equivalent to 4.6 liter/min of dry gas at the same temperature and pressure.


Glass Hopper
Glass Beads + Fly Ash
Level Gage
Vibrator
Cam
20 RPM Clock Motor
Tapping Device
Orifice or Venturi Tube
Oil Manometer
Fine Needle Valve
Gas + Ash + Beads to Prescrubber
Aspirator Tube
Dry Feed Gas Mixture

FLY ASH ADDITION SYSTEM

Figure A-3



APPARATUS FOR OXIDATION AND NO_x STUDIES

Figure A-4

Gas compositions used in the base-line runs were:

		Volume %	
		Dry	Wet
N_2 -SO_2	H_2O	-	7.25
	SO_2	0.32	0.30
	Balance N_2	99.68	92.45
N_2 -SO_2 -CO_2	H_2O	-	7.25
	CO_2	15.85	14.70
	SO_2	0.32	0.30
	Balance N_2	83.83	77.75
N_2 -SO_2 -CO_2 -O_2	H_2O	-	7.25
	O_2	3.02	2.80
	CO_2	15.85	14.70
	SO_2	0.32	0.30
	Balance N_2	80.81	74.95

After completion of the base-line experiments, NO and NO_2 were added to give a total of 0.05% NO_x at various NO/NO_2 ratios. The N_2 content was adjusted in all runs so that the total gas rate was held at 5 liter/min wet. In some runs equimolar quantities of NO and NO_2 were added equivalent to 0.04% NO + 0.04% NO_2.

B. PRESCRUBBER OPERATION

In all runs with a prescrubber, the prescrubber overhead temperature was maintained at $50^\circ C \pm 2$. The gas stream was heated to about $50^\circ C$ with a line heater in runs made without a prescrubber. The prescrubber contained water in the base-line runs in order to saturate the gases with water at $50^\circ C$. In the normal runs, the prescrubber was charged with 7 - 12% sulfuric acid in order to simulate the equilibrium acid concentration that would build up in the prescrubber due to the solution of SO_3 from the flue gases. In several special runs the prescrubber was charged with a solution containing 5.5 wt-% ferrous sulfate plus 7 wt-% H_2SO_4 in order to remove NO_2 from the feed gases.

C. SCRUBBER OPERATION

The majority of the runs were made with a standard sodium sulfite-bisulfite solution similar to the one recommended for the Johnstone process. This solution was made by dissolving reagent grade sodium sulfite and sodium bisulfite in freshly boiled and cooled distilled water and storing the solutions in nitrogen blanketed bottles. The standard solution was made to contain 3.5 moles of Na^+ ion in 100 moles of water. The quantities of Na_2SO_3 and $NaHSO_3$ used were selected so that the SO_2/Na ratio was 0.65. Since the salts contained some $SO_4^=$ and since some oxidation occurred while the solutions were mixed, the $SO_4^=$ content of the lean solutions were always determined just before taking the rich solution samples. In this way the S/C* ratios could be corrected for the amount of $SO_4^=$ present, and the actual quantity of $SO_4^=$ formed in the scrubber could be accurately calculated.

In the runs using the recirculating scrubber, approximately 375 ml of fresh, lean solution was charged to the scrubber. The scrubber was purged with N_2 for 5 minutes to remove air, then heated to 50°C with liquid circulating, after which the desired flue gas flow was started at the normal rate. The overhead gas was sampled and analyzed every 30 minutes. The solution was sampled during and at the end of the run for sulfite and sulfate content. Similar runs were made with selected oxidation inhibitors added to the solution.

In the runs using the once through scrubber, the same compositions of gas and lean solution were used. In this case, however, the lean solution was fed continuously to the column and accumulated at the bottom of the column. The column was started up with the desired flue gas flowing at the normal rate and with the heating jacket adjusted to give 50°C inlet temperature. The lean solution flow was then started at a predetermined rate. Since the liquid hold up in the column was only several minutes and the gas hold up was only a few seconds, the column came to equilibrium in 15 - 20 minutes. The column was then sampled at about 30 minute intervals, usually at varying operating conditions such as slightly different liquid or gas rates, with inhibitor added, etc.

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* See Section IV Appendix A

III. ANALYTICAL METHODS

A. GAS ANALYSES

The scrubber outlet gas was analyzed for SO_2 by bubbling the gas through standard iodine solution containing excess potassium iodide to prevent loss of iodine to the relatively large volume of gas flowing through the bubbler and wet test meter. The excess iodine was titrated with standard sodium thiosulfate solution with starch indicator. The 2.8% O_2 and 0.04% NO were found not to interfere with this SO_2 analysis. The runs with 0.003% NO_2 were also found not to make detectable errors in the SO_2 measurement; however, the runs with 0.04% NO_2 resulted in low SO_2 analyses in the outlet gas, due to the oxidation of the potassium iodide by NO_2.

A relatively simple and accurate colorimetric analytical method for NO_x in flue gases was developed that used a Hach* DR-A 1250 colorimeter and NitraVer IV* powder pillows. A calibration curve was prepared from the results of tests made on a series of solutions containing known concentrations of potassium nitrate in distilled water. This curve was checked by adding known quantities of $SO_4^=$ ion to the standard nitrate samples in concentrations equivalent to the SO_2 present in the flue gas samples. These sulfate values did not appreciably affect the colorimeter readings for nitrate.

The method** is a modification of the phenoldisulfonic acid method for determination of total nitrogen oxides in the presence of SO_2 and ammonia.

The oxides of nitrogen were oxidized to NO_3^-, using an oxidizing solution containing 5 ml of 3% H_2O_2 per 100 ml of 0.1 N H_3PO_4. Phosphoric acid was substituted for sulfuric acid specified in the original procedures to eliminate interference with analyses for SO_2. The SO_2 present in the flue gas was oxidized to $SO_4^=$ at the same time the NO was oxidized to NO_3^-.

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*Manufactured by the Hach Chemical Co., Ames, Iowa.

**Atmospheric Emission from Nitric Acid Manufacturing Processes, Department Health, Education and Welfare, PHS Publ. 989-AP-27, 1966.

The gas sample was drawn into a 1.0 liter bottle containing 25 ml of the oxidizing solution. After measuring the gas pressure and temperature the bottle was shaken for 1/2 hour and allowed to stand overnight. The liquid was then carefully transferred into a beaker, and the bottle washed several times with distilled water which was also added to the beaker. The sample in the beaker was neutralized by addition of 1 N KOH and evaporated to dryness in a 120°C oil bath. The residue in the beaker was then dissolved in distilled water and washed into a volumetric flask. 24 ml of the sample was transferred to a colorimeter bottle, a NitraVer IV powder pillow added, and the bottle shaken for one minute. The nitrate content was determined with the colorimeter after 3 minutes.

B. LIQUID ANALYSES

Liquid samples taken for analysis were carefully blanketed with nitrogen to prevent the normally rapid oxidation of sulfite to sulfate. The sulfate determination was made as soon as the samples were taken. After investigation of existing procedures, a standard turbidimetric method, used for rapid routine tests for sulfate ion in industrial water, was modified and used for these analyses. The sulfate ion is converted to a barium sulfate suspension in the standard method and the resulting turbidity is determined by a photoelectric colorimeter or spectrophotometer. The turbidity is compared to a curve prepared from standard sulfate solutions.

A major source of interference to this sulfate ion determination in the oxidation studies was the presence of sulfite ions which reacted with the barium reagent and formed $BaSO_3$ precipitate. It was necessary, therefore, to eliminate this interference, which was accomplished by adding the sample to concentrated HCl, evaporating the mixture to dryness, and dissolving the residue in water. The HCl liberated the residual sulfite from the sample, thus removing this interference to the sulfate ion determination.

A Hach AC-DR Colorimeter, used for these tests, is equipped with direct reading scales for sulfate (and many other tests). Pre-weighed quantities of reagents were used.

The sulfite concentrations in both the lean and rich solution samples were determined by adding an excess of 0.1 N iodine solution and back titrating with 0.1 N sodium thiosulfate solution to the starch end point. Alkaline solutions were acidified with hydrochloric acid.

IV. CALCULATIONS

The rate of oxidation of SO_2 to $SO_4^=$ in this work was based on the amount of SO_2 being fed to the scrubber in the gas stream and not on the amount of $SO_3^=$ present in the absorbing solution. In all sulfite-bisulfite scrubbing systems there was much more SO_2 equivalent present in the liquid than in the gas phase; however, from the practical standpoint the percentage of the SO_2 in feed gas being oxidized in a commercial scrubber is of interest. The percentage SO_2 oxidized was calculated as follows:

$$\frac{\text{moles/min } SO_2 \text{ oxidized to } SO_4^=}{\text{moles/min } SO_2 \text{ inlet to absorber}} \times 100$$

Concentrations and compositions of the sulfite-bisulfite solutions were represented by C and S, which indicate, respectively, moles of sodium (or other cation) and moles of SO_2 dissolved in 100 moles of water. The actual sulfite concentration is given by C minus S (C-S) and the bisulfite concentration is given by 2S minus C (2S-C). An S/C ratio of 0.5 corresponds to pure sulfite, whereas a ratio of 1.0 corresponds to pure bisulfite. In solutions containing sulfate, the concentration of sodium present as sulfite and bisulfite is represented by C_a, which represents the active base concentration. The $SO_4^=$ concentration is subtracted from the total base concentration to give C_a.

The sulfur material balance was calculated as:

$$\frac{\frac{\text{moles}}{\text{min}}\, SO_2 \text{ in rich sol'n} + \frac{\text{moles}}{\text{min}}\, SO_4^= \text{ in rich sol'n} + \frac{\text{moles}}{\text{min}}\, SO_2 \text{ in outlet gas}}{\frac{\text{moles}}{\text{min}}\, SO_2 \text{ in lean sol'n} + \frac{\text{moles}}{\text{min}}\, SO_4^= \text{ in lean sol'n} + \frac{\text{moles}}{\text{min}}\, SO_2 \text{ in inlet gas}} \times 100$$

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APPENDIX B

DESCRIPTION OF CASES USED IN PHASE III

Case	Description	Flue Gas mmscfm	Exit SO_2 ppm	Coal Requirement tons/hr
1	Large new power plant facility 1400 megawatt	2.5	150	580
2	Large existing power plant facility 1400 megawatt	2.5	150	580
3	Small existing power plant facility 220 megawatt	0.5	300	90
4	New smelter facility (5% SO_2 to scrubber)	0.02*	5,000	-

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*Case 4 was changed during the program to a smelter generating 220,000 scfm (1 atm and 60°F).